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Spatial modulation of molecular adsorption energies due to indirect interaction

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First-principles calculations are used to rationalize the formation of well-separated (~10 Å) molecular rows of phenylglycine upon coadsorption of adenine and phenylglycine on Cu(110) [Q. Chen and N. V. Richardson, Nat. Mater. **2**, 324 (2003)]. It is found that the molecular adsorption leads to long-wave oscillations of the charge density at the Cu(110) surface. The experimentally observed indirect interaction between the molecular rows is mediated by these charge fluctuations. Strain effects, in contrast, are of minor importance.

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The self-assembly of highly organized systems from molecular building blocks opens new avenues for realizing and exploring nanodevice concepts.[1] Typically, metal substrates serve as platforms for the engineering of such supramolecular structures.[2] For the handling of complex molecules on metals, one needs to understand their lateral interactions in dependence on the substrate and coadsorbed species. Experiment and *first-principles* calculations have been very successful in rationalizing the adsorption of single as well as directly interacting molecules on surfaces.[3–8] However, in addition to direct molecular interactions, such as, e.g., H bonds, indirect substrate-mediated interactions between the adsorbates may occur. Although typically smaller than 0.1 eV, they often decisively influence molecular self-assembly and may act at distances beyond 100 Å.[2,9]

Theoretically, long-range adsorbate interactions-mediated substrate electrons were predicted already decades ago.[10] Thereby the interaction energy shows damped oscillations with wavelength π/k_F, where k_F is the Fermi wave vector. This seems to be in accord with a series of observations of indirect adsorbate interactions on the (111) surfaces of Au, Ag, and Cu, e.g., Refs. 1, 9, and 11. At these surfaces partially filled strongly surface localized electronic states with short Fermi wave vectors occur. This is not the case, however, for numerous further systems where similar interactions are observed, see, e.g., Refs. 12–15. The molecular row separation of about ~10 Å on Cu(110) detected in Ref. 14, for example, cannot be explained by Cu Fermi wave vectors between about 1.36 (bulk) and 2 Å^{-1} (thin films).[16] Is the long-range interaction in such cases still due to the response of the substrate electrons?

In order to answer this question, one prototypical system is modeled here on the basis of *first-principles* calculations. We employ density-functional theory (DFT) for simulations of adenine and phenylglycine adsorbed on Cu(110).[14] In this case the presence of indirect interactions between the admolecules is obvious from the adsorption configuration. The present DFT calculations yield a spatial modulation of the molecular adsorption energy that is suitable to explain the experimental findings. The modulation is indeed traced to adsorption-induced oscillations of the surface charge density that in turn lead to a local variation in the substrate-adsorbate bond strength.

Let us start by a brief description of the experimental findings.[14] Adenine deposited on Cu(110) at room-temperature forms ordered one-dimensional molecular dimer chains. Coadsorbed phenylglycine forms double rows that run parallel to the adenine dimer chains, see Fig. 1. The interaction between the adenine dimer row and the neighboring first phenylglycine row is understood in terms of hydrogen bonds, substrate locking, and Coulomb repulsion.[17] Its interaction with the second row of phenylglycine molecules—separated from the first row by ~10 Å—is the subject of the present study. The authors of the experimental study proposed "metal-mediated dipole-dipole interactions" to cause the molecular spacing.

Here the system is modeled using DFT within the generalized gradient approximation (GGA),[18] as implemented in the Vienna *ab Initio* Simulation Package (VASP).[19] The electron-ion interaction is described by the projector-augmented wave (PAW) method,[20] which allows for an accurate treatment of the first-row elements as well as the Cu 3*d* electrons with an energy cutoff of 340 eV. The surface Brillouin zone is sampled using a 1×2×1 mesh. Periodically repeated slabs containing six atomic Cu layers plus the adsorbed molecules and a vacuum region equivalent in thickness to about 17 atomic Cu layers describe the adsystem. This methodology reproduces the measured geometry for phenylglycine adsorbed on Cu(110).[21]

Basically, two mechanisms are conceivable that—possibly in combination—could be responsible for the measured spacing between the two phenylglycine rows: substrate-mediated interactions via long-range strain fields[22] or adsorption-induced Friedel oscillations of the electron density at the metal surface.[10,23,24] By performing calculations where the substrate atoms are either frozen at ideal bulk positions or fully relaxed according to the adsorption-

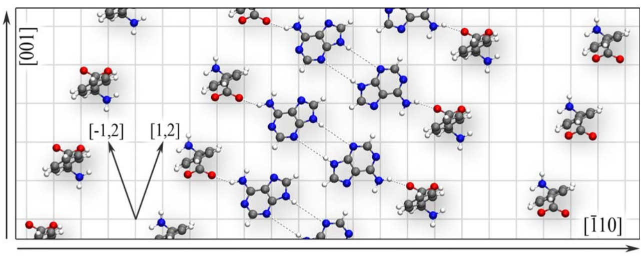

FIG. 1. (Color online) Molecular model derived in Ref. 14 for phenylglycine coadsorbed with adenine forming dimer rows along the 1 and 2 directions on Cu(110). Hydrogen bonds and the Cu(110) surface unit cells are indicated with dashed and gray lines, respectively.

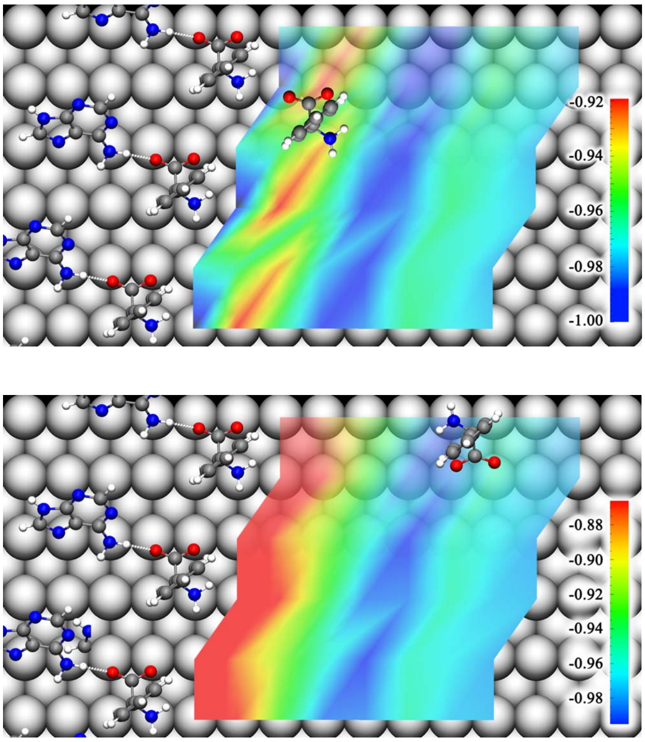

FIG. 2. (Color online) Calculated adsorption energies (in eV, see text) of the second row phenylglycine molecules for parallel (upper panel) and antiparallel (lower panel) orientations in the presence of preadsorbed adenine and phenylglycine. Thereby the leftmost atom of the second row phenylglycine serves as molecular point of reference.

induced forces, one can identify the magnitude of the respective contributions to the spatial modulation of the adsorption energy.

In a first step, we neglect strain effects and vary the distance between the molecular rows without taking the structural relaxations into account. For the calculations we use a model system that includes one adenine and two phenylglycine molecules adsorbed on Cu(110) within a translational symmetry that varies from $\begin{pmatrix}1 & 2\\ 22 & 0\end{pmatrix}$ to $\begin{pmatrix}1 & 2\\ 30 & 0\end{pmatrix}$. The measured scanning tunneling microscopy (STM) data do not allow to conclude unambiguously on the position and orientation of the phenylglycine in the second molecular row with respect to the molecules in the first row. However, given the highly corrugated potential-energy surface (PES) as well as rotational profile for phenylglycine adsorbed on the Cu(110) surface,[21] only two molecular orientations are likely to be relevant. The molecules in the two phenylglycine rows may either be parallel or antiparallel, as shown in the upper and lower panels of Fig. 2, respectively.

The adsorption energy for the second row phenylglycine in the presence of the primary row of phenylglycine/adenine is calculated according to

$$E_{\mathrm{ads}} = E_{\mathrm{tot}} - E_{\mathrm{adn+1pgl}} - E_{\mathrm{pgl}} + \frac{1}{2}E_{\mathrm{H}_2}, \qquad (1)$$

where E_{tot}, $E_{\mathrm{adn+1pgl}}$, E_{pgl}, and E_{H_2} refer to energies of the total system, the adsystem containing adenine and one phenylglycine, phenylglycine, and hydrogen in gas phase, respectively. The corresponding energy surface is shown in Fig. 2. For clarity, the fine structure of the PES (Ref. 21) is suppressed and only the minimum-energy values within the respective Cu(110)(1×1) unit cells are used for the color coding. Obviously, the adsorption energies show damped oscillations with increasing molecular row distance. Depending on the relative orientation of the amino acids, local minima occur for a row distance between about 10 and 14 Å. These seem well suited to explain the experimental finding that "the molecular centers could be closer than 1.28 nm but probably not less than 800 pm."[14] Moreover, the calculated magnitude of the adsorption energy oscillations of ∼100 meV and their wavelength of ∼10 Å are compatible with many experimental examples for indirect interactions.[11–13] Still, on closer inspection, the adsorption energies calculated here do not perfectly reproduce the experimental findings.[14] The calculated global energy minimum does not correspond to separated phenylglycine rows but to the geometry shown in the upper panel of Fig. 2. Here, the phenylglycine molecules are sufficiently close to form hydrogen bonds, similar to the case of phenylglycine monolayers adsorbed on Cu(110).[21]

There are several explanations that possibly account for the discrepancy between experiment and theory in the present case. The perhaps most likely one is related to the modeling of the H bonds. It is discussed in a number of studies, see, e.g., Refs. 25 and 26, that DFT-GGA noticeably overestimates the energy of H-bonds. Based on the same methodology as used here, the cohesive energy of ice Ih was found to be overestimated by 120 meV per molecule.[27] This is of the same order of magnitude as the energy differences relevant in the present case. Further, we cannot exclude that the limited size of our supercell introduces numerical artifacts. In particular the superposition of charge-density waves due to artificial image molecules will affect the accuracy of the calculations. However, the apparent discrepancy between experiment and theory may also be related to the interpretation of the STM micrographs. Additional species not resolved experimentally and not included in the simulations might alter the surface energetics. The adsorption of benzoate on Cu(110), for example, was found to be strongly influenced by naturally occurring or deliberately deposited Cu adatoms.[28]

Regardless of the reasons for the incomplete reproduction of the experimental findings, the calculated adsorption energies compiled in Fig. 2 prove the presence of indirect interactions not related to strain effects. To probe their possible relation to adsorption-induced Friedel oscillations of the charge density, we calculated the difference between the self-consistently obtained charge densities of the adenine and phenylglycine (first row) adsorbed system and the clean Cu surface. The resulting density difference is plotted in Fig. 3. If a Friedel-type behavior of the lateral density oscillations along $[\bar{1}10]$ is assumed $\rho(d) \sim \rho_0 \cos(2k_F d + \Phi)/d^2$, a surface Fermi wave vector $k_F = 0.35$ Å^{-1}—substantially smaller than the bulk value—is obtained from the calculated data. This indicates a strong modification of the Cu surface electronic structure upon molecular adsorption.

The magnitude of the adsorption-induced charge-density

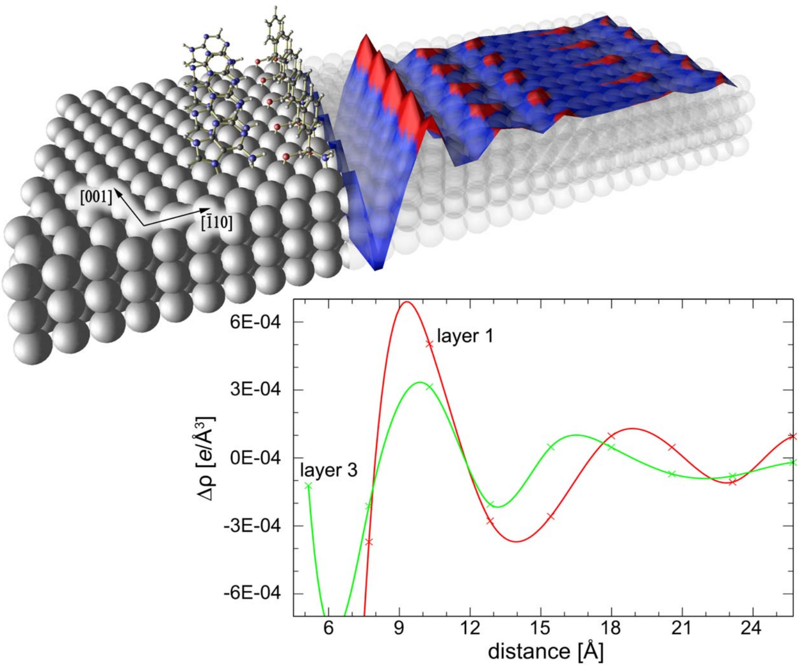

FIG. 3. (Color online) Charge-density difference of adenine and phenylglycine (first row) adsorbed and clean Cu(110) surface. In the upper panel charge accumulation and depletion in the topmost atomic layer are as indicated using the height variation of a corrugated surface. The lower panel shows the density differences in the first and third atomic layers vs the distance from the phenylglycine N atom along the $[\bar{1}10]$ direction.

oscillations is rather small of the order of $10^{-3}e\ \text{Å}^{-3}$. Is this sufficient to explain adsorption energy differences of ~100 meV ? To estimate the influence of the Friedel oscillations on the surface energetics, we follow Harrison[29] and perform molecular orbitals from a linear combination of atomic orbitals (MO-LCAO) calculations. The adsorption of phenylglycine on Cu(110) leads to the formation of covalent bonds between the amino-group nitrogen and the carboxyl-group oxygen with the copper substrate atoms, see Ref. 21. We approximate the variation in the respective bond energies by

$$\Delta E = \Delta q\left(E^{*} - \frac{\epsilon_1 + \epsilon_2}{2}\right), \tag{2}$$

where E^{*} and ϵ_i are the energies of the molecular and atomic orbitals, respectively. The local variation in the charge Δq was calculated from

$$\Delta q = \frac{4}{3}\pi r_{\mathrm{at}}^{3}\Delta\rho, \tag{3}$$

where a radius of $r_{\mathrm{at}}=1.278$ Å has been used to approximate the size of the Cu atom. The O-Cu and N-Cu interaction parameters were calculated within the two-center approximation using the semirelativistic code described in Ref. 30. The resulting bond energy difference vs lateral spacing is shown in Fig. 4. Obviously, the adsorption of phenylglycine on Cu(110) is not perfectly described within the simple tight-binding scheme, as seen from the phase shift between the oscillations calculated within the MO-LCAO model and DFT-GGA. However, given the simplicity of the approximation, the variation in the bond energies calculated within the tight-binding approach agrees surprisingly well with the *first-principles* data. For small distances, the MO-LCAO model tends to overestimate the molecular attraction. This can be explained by the neglect of the repulsive dipole-

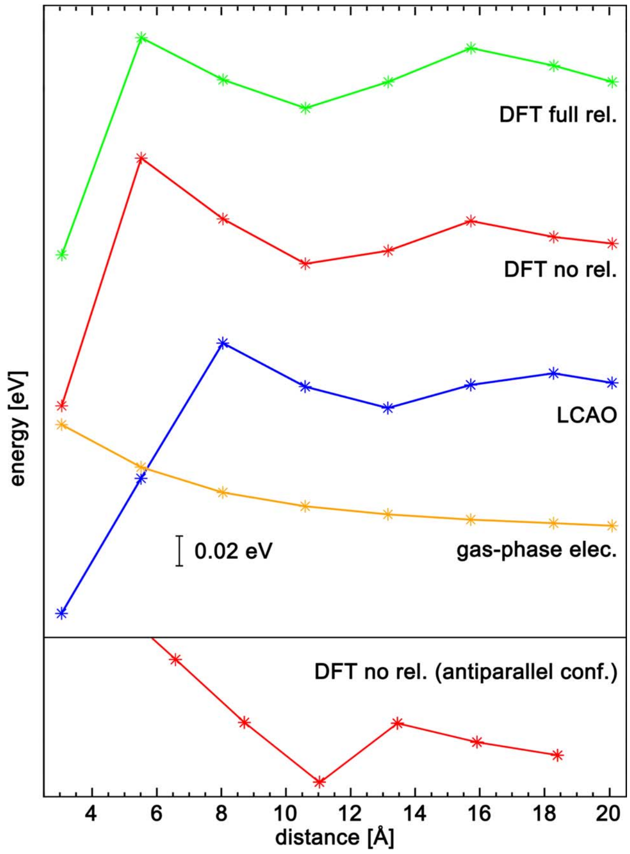

FIG. 4. (Color online) Calculated modifications of the adsorption energy vs lateral spacing resulting from DFT-GGA calculations including structural relaxations, DFT-GGA calculations for frozen adsorbate and substrate, MO-LCAO calculations, and gas-phase dipole-dipole repulsion for the parallel molecular configuration are shown in the upper panel. The lower panel shows the corresponding DFT-GGA data for antiparallel molecular configuration (cf. Fig. 2).

dipole interaction between the phenylglycine molecules (see lowest but one curve in Fig. 4).

The analysis above shows that Friedel oscillations of the surface charge density locally vary the bond strength. In order to see how the density oscillations depend on adsorbate and substrate, we performed calculations for atomic oxygen and nitrogen adsorbed within a (1×36) surface periodicity in the $[\bar{1}10]$ direction. Wave vectors rather similar to the case of the complete molecular row discussed above $k_F^{\mathrm{O}}=0.35\ \text{Å}^{-1}$ and $k_F^{\mathrm{N}}=0.39\ \text{Å}^{-1}$ are determined for Cu(110). The density oscillations are about 50% larger for O than for N atoms. Adsorption on Ag(110) yields Fermi wave vectors that are about 25% shorter, $k_F^{\mathrm{O}}=0.26\ \text{Å}^{-1}$ and $k_F^{\mathrm{N}}=0.30\ \text{Å}^{-1}$. This variation is larger than the difference between the respective bulk Fermi wave vectors, indicating an adsorbate-specific modification of the surface electronic structure.

Until now we have completely neglected the influence of atomic relaxations. How important are strain fields in the context of indirect interactions? The uppermost curve in Fig. 4 contains DFT-GGA results obtained upon fully relaxing both adsorbate and substrate. The differences to the adsorption energies obtained under the assumption that the Cu surface as well as the phenylglycine molecules are frozen are minor and occur basically for molecular distances smaller than ~10 Å. This shows that electronic effects are far more important for long-range indirect interactions than structural effects, at least in the present case. We cross checked this finding by comparative calculations for glutamic acid adsorbed on Ag(110). Here strain effects are slightly more important. While the positions of the local energy minima are still dominated by the electron-density oscillations, the inclusion of structural relaxations is required to obtain the relative depths of the minima in accordance with the measured molecular row spacing of more than 30 Å.[15]

In summary, we used DFT calculations to rationalize the frequently observed long-range order in atomic and molecular adsorption on metal surfaces. Using the model system of adenine and phenylglycine adsorbed on Cu(110), we find local minima in the PES that are suitable to explain the molecular distances observed experimentally. The electronic origin of the indirect interaction in the case studied here is confirmed by (i) MO-LCAO model calculations for the bond strength variation due to charge fluctuations and (ii) calculations with and without structural relaxations that allow for quantifying the influence of long-range strain fields. Our results suggest that mainly surface charge-density oscillations are responsible for the long-range order observed for many atomic and molecular adsorbates on metal substrates, even if no highly surface localized electronic states—as observed at noble-metal (111) surfaces—exist at the clean substrate. The mainly electronic origin of the indirect interactions suggests their tuning by modifying the substrate-adsorbate charge transfer and its screening by the choice of specific adsorbate functional groups and substrates.

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