Long-range repulsive interaction between TTF molecules on a metal surface induced by charge transfer

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The spontaneous formation of self-organized molecular structures at metal surfaces follows a complex balance of interactions between the basic functional units [1]. Attractive short-range forces between molecules are ubiquitous during growth, but their strength and relevance varies depending on the molecular functionalization. For the case of adsorption on metal surfaces these forces compete with substrate-mediated interactions, for example, through elastic stress fields [2] or through surface state electrons [3, 4]. These usually extend for larger length scales than intermolecular dispersion forces and can lead to characteristic quasi-periodic arrays of particles [5, 6]. Long-range interactions can also have a repulsive nature. This is the case of electrostatic interactions between charged particles weakly interacting with a non-conducting host support [11, 12], or in ensembles of organic molecules with large dipolar moments on metal surfaces [13, 14].

Apolar and neutral molecules are not expected to build up long-range interaction potentials other than those mediated by the underlying substrate [10] and, in most cases, attractive dispersion forces lead to nucleation in two or three dimensional condensates. Charge redistribution upon molecular chemisorption is also able of rendering interesting changes in the interaction potentials between molecules [15]. Although this effect is presumably strong in charge transfer adsorbate systems, it has been usually neglected due to the screening nature of metallic substrates. An experimental proof of its relevance in intermolecular interactions is thus still missing. This could also help to build up a quantitative picture about fundamental processes related to molecular charging on metal surfaces.

Here, we report the spontaneous formation of quasiperiodic superlattices of single tetrathiafulvalene (TTF) molecules on a Au(111) surface driven by local charges at the interface induced upon chemisorption. TTF is well known as a prototype donor molecule in charge transfer compounds [17]. The free molecule has no electrical dipole moment. However, on Au(111), it becomes charged upon electron donation. Using a combination of low-temperature scanning tunneling microscopy and density functional theory (DFT) we resolve that a repulsive long-range interaction between charged molecules is built up, thus hindering nucleation in islands. Through the analysis of molecular pair distributions we reconstruct the coverage-dependent intermolecular potential wells forming the molecular lattice.

The experiments were carried out in a custom-made low temperature STM under ultra-high vacuum. An atomically clean Au(111) substrate is exposed to a continuous flux of TTF molecules sublimated from a homemade Knudsen cell. TTF has a very high vapor pressure. To obtain the low coverages used here the crucible was heated to 30°C. The sample temperature was varied during the dosing between 80 K and 300 K, and posteriorly cooled down to the operating temperature of the STM (4.8 K) for sample inspection.

Room temperature deposition of a small amount of TTF (< 0.1 ML) leads to the formation of a characteristic quasi-periodic one-dimensional array of TTF monomers along the FCC regions of the Au(111) 23×√3 reconstruction (Fig. 1). The separation between monomers amounts several nanometers, ∼ 3 nm for the data in Fig. 1(a). This distance is significantly larger than the typical length scale of attractive non-covalent interactions. The formation of the superlattice of TTF monomers needs to be thermally activated. Fig. 1(b) shows the result of dosing TTF on a 80 K cold sample. In this case both monomers and small TTF clusters appear randomly spread and are easily dragged by the STM tip, probably because they populate a weakly adsorbed precursor state. Only upon annealing the molecules self-organize forming the distinctive quasi-periodic array, as
shown in Fig. 1(c). In this case, high-resolution STM images (Fig. 1(d)) of intramolecular structure can be obtained. At negative sample bias we find TTF monomers as composed by four protrusions. The two largest correspond to the 4 sulfur atoms. The other two are fainter tails due to the ethylene ends. TTF appears with a characteristic asymmetry in the images, resembling two of the lateral S atoms being higher than the other two.

Our results clearly indicate that, in the low-coverage limit and after annealing, TTF does not respond to attractive forces like, for example, hydrogen bonding to sulfur atoms [18], avoiding nucleation into islands. Such behavior prevails as the coverage is increased, accompanied by a monotonous decrease in the average pair distance (Fig. 2(a-c)). At 0.08 ML the array is compressed (average pair distance \( \sim 2\text{nm} \)) into double rows of monomers in the FCC regions of the reconstruction. Close to this coverage HCP regions start also to be populated with similar one-dimensional arrays of TTF monomers. Such tendency to avoid nucleation through the formation of quasi-periodic molecular arrays is indicative of a long-range interaction mechanism different from (shorter-range) non-covalent dispersion forces between molecules.

Elastic deformation of the substrate can lead to long-range interactions between adsorbates [2, 3, 5]. The induced stress field can oppose the approach of two adsorbates becoming the driving force of an ordered phase. Indeed, the Au (111) herringbone reconstruction is itself a stressed atomic layer, and therefore, the periodicity of its folding is very sensitive to small changes in the stored elastic energy. Our data show that the herringbone structure is unaffected by a sub-monolayer coverage of TTF. Therefore, this mechanism is improbable in our case. An alternative mechanism for long-range interaction between atoms [7, 8] or molecules [10] on metal surfaces is the interaction potential associated with the Friedel oscillations due to the scattering of surface-state electrons with the adsorbates. A key element in this mechanism is the oscillatory character of the interaction with a period related to half of the electronic Fermi wavelength (\( \lambda_F/2 \)). For Au(111) this corresponds to 1.8 nm, much smaller than the average pair distance of the data in Fig. 1. Furthermore, the average pair distance decreases monotonously with increasing TTF density along the rows (Fig. 2). Thus, an interaction mediated by surface electrons can also be discarded as the driving force leading to the superlattice formation.

Fig. 2(d) shows the pair distance \( r \) distributions of one-dimensional arrays for various coverages (along FCC regions or HCP regions depending on the coverage). For a one-dimensional system of non-interacting particles the first-neighbors’ random pair distribution function \( f_{ran} \)
decays monotonically with the pair distance \( r \) as shown by a dashed line in figure [19]. The peaked distributions in Fig. [2] (d) are symptomatic of a repulsive long range interaction between monomers. Motivated by the donor nature of TTF as a free molecule we have performed \textit{ab-initio} calculations in order to trace back the nature of the molecule-surface interaction and its effect in the long range repulsion between TTF monomers.

We have used density functional theory (DFT) within the generalized gradient approximation [20] as implemented in the VASP code [21] to evaluate the properties of a relaxed layer of TTF on an artificial FCC (111) 4-layers slab of gold atoms. The electron-ion interaction is described by the projector-augmented wave (PAW) scheme [22]. Figure 3(a) shows the resulting structure of a relaxed TTF molecule in a 6×4 unit cell. This large unit cell is employed in order to account for large molecular separations within computationally reasonable limits.

The interaction of the molecule with the surface is driven by local S–Au bonds. Due to the incommensurate dimensions of molecule and surface, the local interactions lead to an asymmetric chemisorption of the molecule. As a result, the molecule aligns along the \{1\overline{1}0\} direction of the surface and tilts 8° with respect to the surface plane. The tilt is responsible of the asymmetry in the experimental constant current STM image, Fig. 1(d), as it is here captured by its Tersoff-Hamman simulation [23] (Fig. 3(b)). At negative bias voltage, the STM image is basically dominated by the shape of the HOMO.

The local interaction character between Au and S atoms implies a sizable bonding strength and a large charge donation into the surface. Indeed, the adsorption energy after dipole corrections is -0.86 eV, and the surface-molecule distance is 2.76 Å. The electronic structure of the S atoms has a large contribution in the highest occupied molecular orbital (HOMO), what causes a large redistribution of electronic charge (Fig. 3(c)). The charge donation is expressed by a partial decrease of the electronic density in the whole molecular plane. The result is a positive charging of the molecule and the creation of a surplus of negative charge localized close to the S–Au bonds. Figure 3(d) shows the planar integration of charge. An excess of positive charge (\sim 0.6 e) is located about the molecule and the corresponding screening negative charge (\sim -0.4 e) is between the molecule and the first atomic layer. The molecule-surface interaction leads to a large surface dipole that is evaluated in Fig. 3(e) according to Ref. [24]. The dipole is zero inside the surface and builds up across the molecule reaching a value of 5.0 D.

The charge donation gleaned from the induced electronic density causes the partial emptying of the HOMO. This is clearly seen by plotting the projection of the full electronic structure onto the molecular orbitals corresponding to the present molecular conformation (Fig. 3(f)) [25]. The molecule-surface interaction also broadens the molecular features associated to the HOMO-1, HOMO and the lowest unoccupied molecular orbital (LUMO), revealing a substantial hybridization with the surface electronic structure, while higher-lying orbitals are thinner showing their small role in the molecular-surface interaction.

The \textit{ab-initio} results evidence a significative charging of the TTF on the Au(111) surface. For pair distances shorter than the Thomas-Fermi screening length on gold surfaces this local charge can build up a repulsive potential between molecules [26]. To evidence its role in the formation of the arrays we analyze the statistics shown in Fig. 2(d). The experimental pair distributions \( f \) arise from the site occupation as dictated by the Boltzmann factor exp(-\( \omega(r) - \mu \))/\( k_B T \), where \( \omega(r) \) is the mean interaction potential behind the formation of the superlattice, \( \mu \) is a (coverage dependent) zeroth order potential [27] and \( k_B \) the Boltzmann constant. To evaluate \( \omega(r) \) we divide the experimental pair distribution \( f \) by that of non-interacting particles (\( f_{ran} \)) and plot \( -\ln(f/f_{ran}) \) (Fig. 4). In the limit of a very dilute system [11] [28], i.e. where no quasiperiodic array is formed, \( \omega(r) \) would
be a good approximation to the (repulsive) pair interaction potential, \( E(r) \). Here, however, \( \omega(r) \) has the shape of a potential well. As the molecular density increases the well becomes more symmetric and shallower, in accord with the TTF molecules being confined into sharper pair distribution and, hence, forming a superlattice. Unfortunately, it is not trivial to obtain the shape of the pair interaction \( E(r) \) from the mean potential \( \omega(r) \). However, we note that for small pair distances \( \omega(r) \) decays as \( 1/r \) and is consistent with an electrostatic repulsion between molecules charged with \( 0.3 \ e \), as it is described in the ab initio results.

Our study has permitted us to show that a highly-ordered chemisorbed phase of single molecules can be formed on a metallic surface as a response to the charge redistribution upon molecular adsorption. Repulsion among localized charges at the molecule/surface region are strong enough to hinder nucleation into molecular islands, even when H-bonding between molecules is expected. We expect similar behavior to occur in other molecular systems, thus being a fingerprint of charge transfer processes at organic/metal interfaces. In this case, the analysis of the nearest-neighbors pair distribution of molecules at different coverages turns out to be a very valuable tool for the study of adsorbates’ interaction potential on metallic surfaces.

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