# Atomic force microscopy contrast with CO functionalized tips in hydrogen-bonded molecular layers: Does the real tip charge distribution play a role?

Michael Ellner,<sup>1</sup> Pablo Pou,<sup>1,2</sup> and Rubén Pérez<sup>1,2</sup>

<sup>1</sup>Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain <sup>2</sup>Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain (Received 6 June 2017; published 14 August 2017)

The interplay of van der Waals (vdW), electrostatic (ES), and short-range (SR) interactions on both the intraand intermolecular contrast observed in high-resolution atomic force microscopy (HR-AFM) is explored in a hydrogen-bonded monolayer of triazine molecules. Our efficient model to simulate AFM images uses the three-dimensional (3D) charge distribution of both tip and sample to calculate the ES interaction, takes into account the tilting of the CO molecule, and reproduces with high accuracy density functional theory calculations. In spite of triazine's hexagonal structure, the intramolecular contrast has triangular symmetry, reflecting the charge density of the molecule. Stripelike intermolecular features, which join the molecules in the H-bond directions, originate from the overlap of the charge density of the atoms in neighboring molecules and are sharpened by the CO tilt. We demonstrate the existence of different potential energy surface minima for the CO tilt and discuss its influence on imaging. Our results clearly show that the ES interaction maps represent a local 3D average of the ES potential of the sample weighted by the tip's charge density, while the SR interaction resembles a local 3D average of the charge density of the sample. However, the strong cancellation of both contributions results in a net interaction dominated by the ES and vdW far from the molecules, and by the SR at short distance. This cancellation, which essentially removes the dependence on the detailed charge distribution of the tip, explains why AFM images can be reproduced using only sample properties such as the z component of the electric field and the charge density of the molecule, and the success of simple models that only incorporate pairwise, point-charge interactions.

DOI: 10.1103/PhysRevB.96.075418

# I. INTRODUCTION

The atomic force microscope (AFM) in the frequency modulation mode, also called noncontact atomic force microscope (NC-AFM), has become the tool of choice to characterize matter at the atomic scale. The functionalization of tips with nonreactive closed-shell atoms or molecules has allowed the unveiling of the inner structure of simple molecules in real space. Since the high-resolution (HR) imaging of a pentacene molecule with a CO tip [1], the AFM has enabled the identification of structures of unknown organic compounds [2], discrimination of covalent bond orders [3], and the imaging of intermediate states of chemical reactions [4,5]. Tip functionalization with inert molecules has also allowed for the imaging for intramolecular features associated with H bonds [6,7]. Moreover, significant steps have been taken toward chemical recognition with the NC-AFM [8,9].

The contrast mechanisms for CO-decorated metallic tips in HR images are nontrivial. Images are usually taken at close tip-sample distance where Pauli repulsion is the dominant interaction and the tip senses high charge density areas. The mobility of the CO molecule or other atom/molecule functionalized tips enhances the potential energy surface (PES) saddle lines and reveals bondlike features in images [10–12]. On polar or ionic surfaces or charged molecules, the electrostatics of the tip can play an important role in enhancing the contrast formation. In our previous work, we have shown that the potential of the CO-metal tip can be represented by the sum of a dipole potential that takes into account the positive charge accumulation of the isolated CO molecule, which exhibits a negative-charge accumulation at the O atom due to

its lone pair [13]. While the electrostatic interaction of the CO molecule with charge sites can provide atomic contrast and the metallic tip cannot, the latter is relevant for spatially extended non-neutral areas [13]. Lastly, on molecules, the van der Waals (vdW) interaction provides an overall attractive background with negligibly atomic-scale fluctuations [8].

Computational calculations have played a key role in understanding the contrast mechanisms of CO tips not only by reproducing the qualitative (and sometimes quantitative) behavior of experimental AFM images, but also by isolating tip-sample interactions. On the one hand, density functional theory (DFT) calculations supplemented by vdW interaction are used to simulate force spectroscopy curves at different sites and, in limited cases, full AFM images. Although accurate and reliable, these are computationally expensive, especially when including tip/sample ionic relaxation. However, if the tip-sample interaction is weak, the effect of the CO tilt can be approximated without carrying out ionic minimization by interpolating the frequency shift of the relaxed probe on a static map using the lateral force acting on the rigid CO molecule [14,15].

On the other hand, AFM images can be calculated using parametrized molecular mechanics (MM) pairwise potentials. The functional form of the force field is typically a Lennard-Jones potential that includes an  $r^{-6}$  term to simulate attractive interactions, mainly vdW, and an  $r^{-12}$  term to simulate repulsive interactions, mainly Pauli repulsion [12,16]. In addition, tip-sample interactions induced by inhomogeneous charge distributions are implicitly accounted for through the Coulombic interactions between a small point charge placed at the probe and the electrostatic potential of the sample [10]. In order to simulate the cylindrical confinement of the CO



FIG. 1. Triazine molecules on graphene. (a) Projected charge density of the isolated triazines at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. (b) SAM adsorbed on a  $(3 \times 3)_G$  unit cell. (c) Total charge density and (d) *z* component of the ES field of the SAM at a height of 3 Å. (Blue: positive; red: negative).

molecule onto the metallic apex, the movement of the probe is constrained by a lateral harmonic potential.

Although these MM models provide a way to rapidly simulate AFM images that account for probe tilt, the results can be misleading. First, the parameters may not be exportable from system to system. Second, the terms that describe the potentials may encompass a variety of interactions. Taking into account the widespread use of these models [10-12,16,17], it is imperative to address the validity of methods that use pointlike tips to simulate AFM images, to understand why they work, and to study their limitations.

The goal of this paper is to understand the role of the tip-sample interactions and probe relaxation on the contrast formation of the intra- and intermolecular features observed on HR-AFM images of simple molecules. To this end, we extend the method developed in [13] to rapidly simulate and interpret HR-AFM images of molecules acquired with functionalized tips retaining DFT accuracy. The method takes into account the charge distribution of the probe, the ES potential of the sample, and the tilt of the probe atom/molecule. We have simulated images of a self-assembled monolayer (SAM) of s-triazines (C<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, hereafter triazine) on graphene (G). Each triazine molecule is a six-member ring with alternating C-N atoms [Fig. 1(a)] that bind into a SAM via H bonds and are physisorbed onto the G. The system is an ideal testbed for studying the contrast mechanism of CO-decorated tips on molecules. On the one hand, triazine offers different chemical elements and an inhomogeneous charge distribution. On the other hand, the G substrate, in addition to being a technologically rich material whose electronic properties can be tuned by the adsorbed SAM, interacts weakly with the triazine molecules, thus allowing for a SAM formation with negligible corrugation.

This work is organized as follows: First, we briefly describe the methods used to simulate HR-AFM images (Sec. II) and the system that it is applied to (Sec. III A): a triazine SAM on graphene probed by a CO tip. Then, the DFT results obtained for this system and used to parametrize the model will be outlined (Sec. III B). Subsequently, through static force-decomposed maps and frequency-shift HR-AFM images, we discuss the contrast mechanism of the molecular, intramolecular, and intermolecular regions as a function of the tip-sample distance (Sec. III C). This is of the outmost importance for the interpretation of AFM experiments. Finally, the existence of different PES minima for the CO tilt will be discussed along with its influence on both theoretical and experimental imaging.

#### **II. METHODS**

## A. HR-AFM image simulation method

We propose a method to simulate interaction-decomposed HR-AFM images with DFT accuracy [13]. The model separates the total tip-sample interaction into a van der Waals (vdW), electrostatic (ES), and short-range (SR) contribution and accounts for the penalty of a functionalized tip rotation (tilt). Given an initial tip position  $\vec{R}_{tip}$ , the coordinates of the probe are obtained by minimizing the potential,

$$V(R_{\rm tip},\theta,\varphi) = V_{\rm ES} + V_{\rm SR} + V_{\rm vdW} + V_{\rm tilt},$$
 (1)

for the polar and azimuthal rotation angles ( $\theta$ ,  $\varphi$ ) of the probe. The HR-AFM energy, force, and frequency-shift images at a given tip height are obtained by determining the probe positions that minimize Eq. (1) on a two-dimensional (2D) grid, and evaluating the corresponding total energy, its gradient, and the second-order derivative with respect to the *z* direction [18], respectively.

The electrostatic interaction is calculated from

$$V_{\rm ES} = \int \rho^{\rm probe}(\vec{r}, \vec{R}_{\rm tip}, \theta, \varphi) \phi^{\rm sample}(\vec{r}) d\vec{r}^3, \qquad (2)$$

where  $\rho^{\text{probe}}$  is the charge density of the probe and  $\phi^{\text{sample}}$  is the ES potential of the sample. These are obtained on a 3D real-space grid from separate DFT calculations (see Sec. II B for details): one for the sample, and one for the probe in an upright position, and with the tip placed at  $\vec{R}_{\text{tip}} = \vec{0}$ . The ES interaction is then calculated at an arbitrary position  $\vec{R}_{\text{tip}}$  and rotation ( $\theta, \varphi$ ) by interpolating the charge density of the probe.

The short-range interaction, which incorporates mainly Pauli repulsion but also charge redistribution effects, is fitted to a sum of pairwise Morse potentials. The fit is done on the SR component of system-specific tip-sample DFT energy vs distance calculations without ionic relaxations. The contribution is isolated by subtracting the ES interaction, computed as with Eq. (2), from the Kohn-Sham (KS) energy (the DFT energy without vdW interaction),

$$V_{\rm SR} = E_{\rm KS} - V_{\rm ES}.$$
 (3)

The approximated DFT energy is supplemented using a semiempirical vdW approach. Specifically, we use Grimme's DFT-D3 theory [19], which for AFM calculations complements well the KS energy [20].

Lastly, the potential  $V_{\text{tilt}}(\theta, \varphi)$  accounts for the penalty of a probe tilt. For a CO tip with polar symmetry, an angular spring potential,

$$V_{\text{tilt}} = \frac{1}{2} \kappa \theta^2, \qquad (4)$$

with  $\kappa = 0.01$  Ha/rad<sup>2</sup> has been previously reported to reproduce experimental results [10,12,13,16].

## **B.** Computational details

All DFT calculations were carried out with the project augmented wave (PAW) function method as implemented in VASP [21] using a  $7 \times 7 \times 1$  Monkhorst-Pack grid for the Brillouin zone integration, a 600 eV plane-wave cutoff, a  $10^{-6}$  eV accuracy electronic self-consistency loop, and the Perdew-Burke-Ernzerhof (PBE) exchange and correlation (XC) functional [22] supplemented by vdW DFT-D3 [19]. The ES potential of the sample and charge density of the probe used in Eq. (2) were calculated on a uniform 3D mesh of  $\lambda \approx 0.075$  Å spacing with the dipole correction applied to the *z* direction to eliminate spurious interactions among the repeated unit cells.

Geometrical positions of the SAM were obtained through DFT ionic relaxation of all triazine atoms of a SAM on a (3 × 3)<sub>G</sub> supercell of  $6.53 \times 6.53 \times 43.4 \text{ Å}^3$  using the conjugate gradient algorithm until the residual force on each atom was less than  $F_{\rm min} = 0.01 \text{ eV/Å}$ . The unit cell (3 × 3)<sub>G</sub> optimizes the binding energy of the molecule to the G. The calculated adsorption distance was 3.33 Å and the binding energy per molecule was 405 meV. The molecules are adsorbed with negligible corrugation and form a triangular array with a 6.53 Å separation between molecules [Fig. 1(b)]. The SAM induces a small rotation of the preferred adsorption sites of the isolated triazines on the G: the C atoms of the triazine on top of the G's C atoms. Triazine has been experimentally synthesized on a G/Pt(111) substrate [23], which is a weakly interacting G-metal system with a tiny corrugation [20].

All HR-AFM images computed from Eq. (1) were calculated on a 2D mesh with  $\lambda = 0.1$  Å spacing. Gradients with respect to the rotation angles, computed analytically, were used to more readily converge the probe rotation. The probe position was relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm until the generalized gradients were less than  $10^{-4}$  au. As we justify in Sec. III C, our calculations neglect the contribution coming from the metallic part of the tip.

# **III. RESULTS AND DISCUSSIONS**

#### A. Sample characterization

Here, we apply the method described above to simulate HR-AFM images of a triazine self-molecular assembly on graphene probed by a CO tip. Each triazine is an aromatic



FIG. 2. DFT force vs distance calculations of a triazine SAM/G probed by a CO molecule. (a) Scheme of sites. (b) DFT results of all the sites. (c) Total (TOT) force and electrostatic (ES), van der Waals (vdW), and short-range (SR) force contributions on the N site.

six-member ring molecule with alternating C-H and N atoms [Fig. 1(a)]. They bind into a triangular lattice SAM via C-H  $\cdots$  N hydrogen bonds (H bonds) and are physisorbed onto the G [Fig. 1(b)]. Although triazines can be grown on other substrates [24,25], graphene, with its very low reactivity, promotes the formation of well-ordered layers with no chemical coupling to the SAM [26,27]. Thus, this 2D system is ideal to study the contrast formation of the AFM with functionalized tips: the SAM is flat and thus removes corrugation effects. In addition, it presents three types of

chemical species and it has both covalent intramolecular coupling as well as intermolecular coupling through H bonds.

Figures 1(c) and 1(d) show the charge density and the z component of the ES field of the triazine SAM/G at a plane z = 3 Å from the surface. The charge density has a triangular shape coming from the dominant N lone pairs [see  $\rho(\vec{r}, E = E_{\rm HOMO})$  in Fig. 1(a)]. These also dictate the form of the z component of the ES field. It is attractive towards electrons inside the molecule and repulsive outside, with the repulsive centers created by the lone pairs of the N atoms. Although the charge density of the SAM is very similar to the one of the isolated triazine molecules, there are faint intermolecular features present in the charge density far from the plane of the substrate or charge redistribution of the SAM (both of which are negligible [28]), but to the overlap of the C-H ··· N electronic densities of neighboring triazine molecules.

### **B.** Force spectroscopy

In order to simulate HR-AFM images with the method described in Sec. II A, the SR Morse parameters are first fitted to DFT calculations. To this end, DFT+vdW force vs distance calculations keeping the CO molecule fixed are performed on the CO tip-triazine SAM/G sample system. The tip is placed on eight sites of the SAM [Fig. 2(a)]: above N, C, and H atoms, in between bonded atoms of the triazine C-H, N-C, and C-C, in the center of the molecule (cent), and in two intermolecular regions (H bond and inter). As the tip approaches the sample, the total force is first attractive and then repulsive [see Fig. 2(b)]. The N site exerts the highest repulsion for tip-sample distances z < 3.6 Å and comparable to other high-density C, C-C, and C-N sites. Although the center of the molecule does not have high electron density, it is the fourth most repulsive site. The C-H site yields very similar forces to the center site, and the H and H-bond sites are less repulsive. Finally, the intermolecular region with the least electronic density (intersite) yields the weakest force; it is the only site still attractive at z = 2.5 Å. Each of these tip-sample interactions can be decomposed into ES, vdW, and SR components. Figure 3(c) shows the decomposition on the N site. Due to the overlap between the CO and triazine wave functions, the SR force (mostly originated from Pauli repulsion) grows exponentially as the tip-sample distance decreases. Likewise, due to the overlap of electronic densities, a similar rate of decay (growth in magnitude) occurs in the ES force. This results in a strong cancellation between these two, with the SR dominating at small tip-sample distances (z < 3.2 Å). Nevertheless, for z > 4.0 Å, the vdW is the dominant interaction. It is also worth noting that it is the only interaction that is affected by the presence of the G substrate. That is, for all other interactions, the CO tip-triazine SAM/G and the CO tip-triazine SAM are equivalent. This is in accordance with the large decay in the magnitude of the SR and ES forces with increased tip-sample distance.

From the DFT force vs distance calculations, the SR interaction is extracted using Eq. (3) [markers in Fig. 3(a)] and fitted to pairwise Morse potentials between a Morse center placed at the tip apex (O atom) and centers placed in the sample's plane [lines in Fig. 3(a)]. Admittedly, the large growth



FIG. 3. Parametrization of the AFM simulation model using four species (N, C, H, and cent) and three species (N, C, and H). The markers are the DFT input data and the lines are the results of the models. (a) Parametrization of the SR force using the four-species model. Total force obtained with the (b) four-species model and (c) three-species model.

of the SR force complicates the modeling of the interaction through pairwise potentials. The strong cancellation between the SR and ES force requires a high-precision parametrization. We find that using three species of Morse centers, i.e., one for each distinct atomic species (N, C, H), and placing the centers at the atomic positions of the triazine SAM is not enough to reproduce the rich contrast of Fig. 2(b). This can be appreciated in Fig. 3(c) where the total DFT force (markers) and the model's force (lines) are plotted. The problem is solved by augmenting the variational freedom of the fit by adding a ghost Morse species to the center of the hexagons of the triazines.



FIG. 4. Static force decomposed AFM images of a triazine SAM/G probed by a CO tip. From left to right, the total (TOT), electrostatic (ES), van der Waals (vdW), and short-range (SR) force maps for five tip heights (top to bottom). Scale bars correspond to 2 Å. The gray scales correspond to the minimum (dark) and maximum (bright) value of the interaction shown in the bottom-left corner of each image.

This improves the precision of the fit and provides an excellent agreement between the DFT and the model's results for the full range of tip-sample distance [see Fig. 3(b)]. Possibly, the need for a ghost species comes from the lack of directionality of the Morse potential that may be important when modeling aromatic molecules. Namely, they have  $\sigma$  and  $\pi$  bonds that make the directionality of the charge density relevant. Note that no Morse centers are placed in the plane of the G. As stated before, for this system, the substrate does not play any role in the SR interaction.

# C. HR-AFM images

After achieving an excellent fit to the DFT calculations, interaction-decomposed images without tip relaxation are simulated. These are key to understand the contrast mechanism of the CO tip. Figure 4 shows the static maps (without probe relaxation) for five tip-sample distances from z = 2.87 Å to z = 3.93 Å. In order to highlight the contributions, the gray

scale in each plot is fixed by the maximum and minimum value of the interaction. For large tip-sample distances (z > 3.6 Å). the attractive vdW and ES interactions dominate and make the inside region of the molecule the most attractive feature of the image. The ES maps have a triangular shape at the molecules with the vertices at the C atom positions. In contrast, the SR is repulsive and partially cancels the ES contribution. In these maps, the molecule is the most repulsive part and images also have triangular features but with vertices around the N atoms. The net interaction has dark (attractive) features at the triazine positions with a triangular shape given by the remnant ES and vdW interactions. As the tip-sample distance decreases, the SR-ES cancellation leans in the direction of the repulsive SR interaction. On the other hand, the vdW contrast becomes negligible (see contrast range values in Fig. 4). This leads to a change in contrast of the total force with bright (repulsive) features around the N atoms of the molecules. At very small tip-sample distances, z < 2.9 Å, very faint intermolecular features appear both in the total force



FIG. 5. Simulated AFM images of a triazine SAM/G probed by a CO tip. The first column is the total force, the second column is the reduced frequency shift (-dF/dz), and the arrows in the third column show the lateral relaxation of the CO probe. Scale bars correspond to 2 Å.

and SR contribution. These can already be appreciated in the charge density of the SAM [see Fig. 1(c)] and originate from the spatial overlap of the C-H $\cdots$ N outermost electrons of adjacent triazine molecules [15,29].

It has been proposed that the contrast in AFM images may be explained exclusively from sample-related properties, such as the electronic density or the associated electric field [15,30–35]. However, in our calculations, for all tip-sample distances, the ES force does not exactly resemble the zcomponent of the ES field of the SAM. For large distances, z > 3.6 Å, it has attractive triangular features with vertices at the C-H's of the triazines. As the distance decreases, the features become more hexagonal and follow the perimeter of the molecule. The effect reflects the nonlocalized nature of the CO molecule's charge distribution. That is, the ES interaction is a 3D average of the ES potential of the sample weighted by the CO nonspherical charge distributions. Similarly, the SR contribution does not exactly resemble the charge density of the SAM. For large distances, z > 3.6 Å, it also has repulsive triangular features but with vertices at the N atoms. Even though the N atoms have more localized charge density than the C atoms, the SR repulsive feature also merges into hexagons as the tip-sample distance decreases. This also indicates that the interaction resembles not just a z average of the charge density of the outermost electrons of the sample [15,36], but a 3D average. It also explains why the centers of the molecule have high repulsion even though the electronic density is low. Surprisingly, when both SR and ES contributions are joined, the 3D averaging effect seems to be reduced. At large tip-sample distances, z > 3.6 Å, the total force appears more like the *z* component of the ES field [Fig. 1(c)] than the ES interaction map. Similarly, at small tip-sample distances (z < 3.2 Å), the total force resemblance to the charge density of the SAM [Fig. 1(d)] is greater than the SR resemblance to the charge density.

The SR-ES strong cancellation also explains why pointlike methods to simulate HR-AFM images reproduce qualitatively (or even quantitatively) the experimental images or the more accurate DFT simulations. In these methods [12,16], the averaging effects of the tip are not explicitly included. Nevertheless, as a result of the cancellation, the potential energy landscape (PES) can be fitted to a polynomial ( $R^{-n}$ ) potential, i.e., Lennard-Jones. Also, the induced effect of the sample's charge distribution differences can be incorporated with a pointlike approach to the ES contribution [10].

Note that in the maps shown in Fig. 4, the contribution coming from the metallic part of the tip (the apex that the CO is attached to) has been neglected. As described in [13], the metallic tip can be modeled by a dipole of the order of 1.00 D placed at the metal apex. On the triazine SAM/G, the associated force varies from 0.75 to 2.43 pN for tip-sample distances 3.93 and 2.87 Å. It represents a maximum of 2.5% of the total contrast.

With the insight gained by understanding the origin of the tip-sample interaction, we are now in a position to discuss the effect of the tip tilt [1,3,16,32] on the HR-AFM images, the underlying interaction that controls it, and its effect on the imaging of intermolecular features [6]. Figure 5 shows the total force, frequency shift, and relaxation maps of the probe. Due to attraction coming from the ES and vdW interactions in the center of the molecules, there is a slight tilt of the CO tip towards the molecules  $\sim 0.3$  Å at z = 3.7 Å. However, for large tip-sample distances, z > 3.6 Å, the total force is barely perturbed by the tip and resembles the z component of the ES field. At intermediate tip-sample distances, z < 3.6 Å, the relaxation induced by high electronic density sites, i.e., C, N, and covalent bonds, defines the contour of the molecule [1,3] and results in a sharpening of the triangular stripes seen in the static maps. The characteristic triangular shape displayed by the triazine is due to the large electronic density of the N atoms compared to the C-H groups, even far from the molecule [Fig. 1(c)]. Notice that the behavior of the N atoms in the triazine differs from what has been observed in large molecules with several six-member rings and containing only a very few N atoms [37,38]. In that case, the electron density coming from the C atoms decays more slowly than the N's, resulting in weaker repulsion at the N atoms compared to the C atoms.

The relaxation, which is shown more explicitly in Fig. 6, is significant for intermediate to small tip-sample distances (z < 3.6 Å), where the SR repulsion overpowers the other interactions. Due to increased electronic density, the relaxation is dominated by the N atoms. Consequently, the CO starts tilting near the N site at larger tip-sample distances compared



FIG. 6. Lateral tilt distance of the CO probe along two profiles of a triazine SAM/G and for four tip heights. (a) A profile along the x direction from the center of a triazine molecule to the center of a neighboring molecule and passing through C, H, and N atoms. (b) A profile along the y direction from an H-bond region to the center of a triazine molecule and passing through a N-C bond.

to other sites. Also, outside of the molecules, the CO tilts away from the N atoms and towards the neighbourhood of the C-H groups. Finally, we consider the effect of the vdW interaction on the CO tilt. For an isolated molecule, the vdW attraction causes a tilt towards the molecule [3]. However, in the SAM, the lateral attractive vdW interaction in the middle of the intermolecular space, which results from the contribution of all the neighboring molecules, cancels out and has a very minor effect on the CO tilt.

At small tip-sample separations, z < 3.2 Å, the CO tilt enhances the ripples connecting the triazine molecules in the H-bond directions [6,16]. Although they are weakly apparent in the charge density and static maps, the ripples are augmented at this distance range (see Fig. 5). In this case, the relaxation is dominated by the slowly decaying charge density of the N atoms. It softens the high-repulsion areas induced by the molecules, that is, the intramolecular areas, and renders visible the intermolecular features [15,29]. Notice that these are not shaped as linear stripes (sharpening of the saddle lines), but



FIG. 7. Energy landscape of CO probe on triazine SAM/G. (a) Energy profile along the reaction coordinate of the CO movement with the probe placed 1 Å away from an N atom in the direction of the H bond. (b),(c) Energy maps with respect to the polar angle ( $\theta$ ) and the azimuthal angle ( $\varphi$ ) on the same tip position as (a). Simulated AFM images at z = 3 Å with (d) top-to-bottom and (e) bottom-to-top relaxation.

instead have a faint triangular shape. This is produced by the particular relaxation pattern around the C-H area created primarily by the two neighboring N atoms. This discussion shows that the appearance of the ripples is linked with the PES. Forces are very weak at the intermolecular region ( $\sim$ 100 pN) and we do not expect the associated ionic relaxation (not considered in our calculations) to significantly change the structure and symmetry of the PES and, thus, the appearance of the ripples.

As explained before, for large tip-sample distances (z > 3.6 Å), the CO tilt direction is dictated by the vdW and ES interactions. These always attract the probe towards the molecule. Conversely, as the distance decreases, the SR interaction creates a barrier that pushes the probe away from the molecule. The change of regime suggests that the relaxation

PES of the probe is complex. Indeed, here we point out the existence of different PES minima of the CO tip at both sides of the triangular contour of the molecules. For instance, at a tip lateral distance of 0.95 Å from the N atom in the direction of the H bond, the relaxation PES has two minima for a range of tip heights. These are shown in Fig. 7(a) where the tip-sample energy as a function of the reaction coordinate, defined as the CO's lateral displacement along the minimum-energy path obtained by varying the probe tilt angle, is plotted for three different tip heights. The zero of the reaction coordinate corresponds to the CO in an upright position and the positive values correspond to displacements towards the N atom. The full PES for two tip-sample distances are shown in Figs. 7(b) and 7(c). The PES at z = 2.8 and z = 3.0 Å have two minima and, in contrast, the PES at z = 3.2 Å has only one. This is explained by the growth of the SR barrier around the molecule as the tip-sample distance decreases (see Fig. 4), which produces an even-degree polynomial relaxation PES with two turning points. This may have important consequences for HR-AFM image simulations, that is, different images may be obtained depending on the energy minimization procedure, e.g., local vs global minimum search or initial conditions. For instance, in the present case, if maps are calculated from top to bottom, that is, the rotation angles obtained from the minimization of a higher tip distance are used as initial conditions, the probe would always relax towards the molecule. On the other hand, if maps are calculated from bottom to top or if a global minimization algorithm is used, at small tip heights the probe would relax away from the molecule. As shown in Figs. 7(d) and 7(e), this would lead to different HR-AFM images.

The trapping of the probe on a PES minimum should also be factored into the interpretation of experimental images where the experimental settings, e.g., temperature, scan mode, etc., may cause alterations in the measurements of bond lengths and bond orders. This could be especially important in systems with large ES interaction, for instance, in polar or ionic samples, or with charged functionalized tips, e.g., a Xe metallic tip.

#### **IV. CONCLUSIONS**

We have proposed a model to rapidly simulate interactiondecomposed HR-AFM images with DFT accuracy. The model PHYSICAL REVIEW B 96, 075418 (2017)

is parametrized through DFT calculations and decomposes the total tip-sample interactions into SR, vdW, and ES contributions. The latter takes into account the charge distribution of both the tip and the sample. We have used the method to study the imaging of a triazine SAM by a CO tip. We have shown that the ES interaction maps a 3D average of the sample's z component of the ES field, while the SR interaction maps a 3D average of the sample's charge distribution. The strong cancellation between the SR and ES contribution in the final, total interaction results in (1) a reduction of the 3D averaging effects and (2) a less pronounced repulsive total interaction at small tip-sample distances (compared to Pauli's). For large tip heights, the resulting total interaction resembles the z component of the ES field of the sample. In contrast, for small tip heights, it resembles the charge distribution. The strong cancellation also explains why simple pairwise pointlike models qualitatively reproduce the HR images.

Strikingly, HR-AFM images of the triazine present a strong asymmetry between the C and N atoms, with the latter being more repulsive at small tip heights. The tilt of the CO tip highlights the triangular contour of the N atoms and, at very small tip heights, intermolecular features (H bonds). These stripes, due to relaxation towards the C-H groups induced by repulsion from the neighboring N atoms, have a triangular shape. We attribute their appearance to (1) the overlap of the electronic densities of the C-H and N atoms involved in the H bond, and (2) their enhancement upon the tip tilt to a lowering of the overall contrast.

We have also examined the 3D PES of the CO tip in the SAM and point to the existence of two minima at the contour of the triazine. This may have observable consequences, both theoretical and experimental, on the distortion of the image, and the comparison of images obtained via different scan modes.

## ACKNOWLEDGMENTS

We thank the Marie Curie ITN Network ACRITAS (Grant No. FP7- PEOPLE-2012-ITN-317348) and the Spanish Ministerio de Economía y Competitividad (MINECO, Project No. MAT2014-54484-P) for financial support.

- L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, Science 325, 1110 (2009).
- [2] L. Gross, F. Mohn, N. Moll, G. Meyer, R. Ebel, W. M. Abdel-Mageed, and M. Jaspars, Nat. Chem. 2, 821 (2010).
- [3] L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitian, D. Peña, A. Gourdon, and G. Meyer, Science 337, 1326 (2012).
- [4] D. G. de Oteyza, P. Gorman, Y.-C. Chen, S. Wickenburg, A. Riss, D. J. Mowbray, G. Etkin, Z. Pedramrazi, H.-Z. Tsai, A. Rubio, M. F. Crommie, and F. R. Fischer, Science 340, 1434 (2013).
- [5] F. Albrecht, N. Pavliček, C. Herranz-Lancho, M. Ruben, and J. Repp, J. Am. Chem. Soc. 137, 7424 (2015).

- [6] J. Zhang, P. Chen, B. Yuan, W. Ji, Z. Cheng, and X. Qiu, Science 342, 611 (2013).
- [7] A. M. Sweetman, S. P. Jarvis, H. Sang, I. Lekkas, P. Rahe, Y. Wang, J. Wang, N. R. Champness, L. Kantorovich, and P. Moriarty, Nat. Commun. 5, 3931 (2014).
- [8] N. Pavliček and L. Gross, Nat. Rev. Chem. 1, 5 (2017).
- [9] B. Schuler, Y. Zhang, S. Collazos, S. Fatayer, G. Meyer, D. Perez, E. Guitian, M. R. Harper, J. D. Kushnerick, D. Peña, and L. Gross, Chem. Sci. 8, 2315 (2017).
- [10] P. Hapala, R. Temirov, F. S. Tautz, and P. Jelínek, Phys. Rev. Lett. 113, 226101 (2014).
- [11] S. K. Hämäläinen, N. van der Heijden, J. van der Lit, S. den Hartog, P. Liljeroth, and I. Swart, Phys. Rev. Lett. 113, 186102 (2014).

- [12] M. P. Boneschanscher, S. K. Hämäläinen, P. Liljeroth, and I. Swart, ACS Nano 8, 3006 (2014).
- [13] M. Ellner, N. Pavliček, P. Pou, B. Schuler, N. Moll, G. Meyer, L. Gross, and R. Pérez, Nano Lett. 16, 1974 (2016).
- [14] C.-S. S. Guo, M. A. Van Hove, X. Ren, and Y. Zhao, J. Phys. Chem. C 119, 1483 (2015).
- [15] C.-S. Guo, X. Xin, M. A. Van Hove, X. Ren, and Y. Zhao, J. Phys. Chem. C 119, 14195 (2015).
- [16] P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov, and P. Jelínek, Phys. Rev. B 90, 085421 (2014).
- [17] N. J. van der Heijden, P. Hapala, J. A. Rombouts, J. van der Lit, D. Smith, P. Mutombo, M. Švec, P. Jelínek, and I. Swart, ACS Nano 10, 8517 (2016).
- [18] R. García and R. Pérez, Surf. Sci. Rep. 47, 197 (2002).
- [19] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. 132, 154104 (2010).
- [20] B. de la Torre, M. Ellner, P. Pou, N. Nicoara, R. Pérez, and J. M. Gómez-Rodríguez, Phys. Rev. Lett. 116, 245502 (2016).
- [21] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
- [22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [23] B. de la Torre, Ph.D. dissertation, Universidad Autónoma de Madrid, 2015.
- [24] A. J. Martínez-Galera and J. M. Gómez-Rodríguez, J. Phys. Chem. C 115, 11089 (2011).
- [25] D. Wang, Q.-M. Xu, L.-J. Wan, C. Wang, and C.-L. Bai, Langmuir 18, 5133 (2002).
- [26] A. J. Martínez-Galera and J. M. Gómez-Rodríguez, J. Phys. Chem. C 115, 23036 (2011).

- [27] A. Martín-Recio, A. J. Martínez-Galera, and J. M. Gómez-Rodríguez, J. Phys. Chem. C 119, 401 (2015).
- [28] The maximum charge transfer with the substrate is  $1.4 \times 10^{-6} \text{ e/Å}^3$  and in the intermolecular region is  $2.0 \times 10^{-7} \text{ e/Å}^3$ . The maximum charge transfer due to the presence of neighboring triazine molecules is  $1.25 \times 10^{-4} \text{ e/Å}^3$  and in the intermolecular region is  $6.5 \times 10^{-6} \text{ e/Å}^3$ .
- [29] A. J. Lee, Y. Sakai, M. Kim, and J. R. Chelikowsky, Appl. Phys. Lett. 108, 193102 (2016).
- [30] D. Drakova, Reports Prog. Phys. 64, 205 (2001).
- [31] M. Emmrich, F. Huber, F. Pielmeier, J. Welker, T. Hofmann, M. Schneiderbauer, D. Meuer, S. Polesya, S. Mankovsky, D. Ködderitzsch, H. Ebert, and F. J. Giessibl, Science 348, 308 (2015).
- [32] N. Moll, L. Gross, F. Mohn, A. Curioni, and G. Meyer, New J. Phys. 12, 125020 (2010).
- [33] C. S. Guo, M. A. Van Hove, R. Q. Zhang, and C. Minot, Langmuir 26, 16271 (2010).
- [34] N. Moll, L. Gross, F. Mohn, A. Curioni, and G. Meyer, New J. Phys. 14, 083023 (2012).
- [35] C.-G. Wang, Z.-H. Cheng, X.-H. Qiu, and W. Ji, Chin. Chem. Lett. 28, 759 (2017).
- [36] N. Moll, B. Schuler, S. Kawai, F. Xu, L. Peng, A. Orita, J. Otera, A. Curioni, M. Neu, J. Repp, G. Meyer, and L. Gross, Nano Lett. 14, 6127 (2014).
- [37] B. Schuler, S.-X. Liu, Y. Geng, S. Decurtins, G. Meyer, and L. Gross, Nano Lett. 14, 3342 (2014).
- [38] N. Kocić, X. Liu, S. Chen, S. Decurtins, O. Krejčí, P. Jelínek, J. Repp, and S.-X. Liu, J. Am. Chem. Soc. 138, 5585 (2016).