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First-principles analysis of STM image heights on Si(100)

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We report on theoretical investigations of STM image heights on Si(100). Calculations are performed using density functional theory (DFT) within the Keldysh non-equilibrium Green's function (NEGF) formalism. The non-equilibrium potential drop between Si(100) and a scanning tunneling microscope (STM) tip is determined self-consistently. This potential drop is found to play an important role in the calculated image height characteristics of adsorbed hydrocarbons, by lowering the vacuum barrier and shifting molecular levels. Numerical data are collected for image heights of styrene against a hydrogen passivated Si(100) background, and agree quantitatively with the corresponding experimental results. We also present a comparison between results obtained by the NEGF-DFT formalism and the Tersoff-Hamann approximation, showing that non-equilibrium analysis can be important in the study of STM image heights of molecules.

I. INTRODUCTION

As technology continues to advance towards atomic dimensions, the scanning tunneling microscope (STM) is increasingly utilized in the study of devices on this scale. Various effects including radiative emission, negative differential resistance, switching, and charge regulation have been observed at atomic dimensions.[1–5] There is a strong need to characterize distance dependent bonding properties between a proto-device and a STM tip during current-voltage measurements.[6] This is necessary for properly evaluating device performance since STM current measurements can differ by several orders of magnitude depending on the distance between the tip and sample. On semiconductor surfaces such as the silicon surface, this is however a rather complicated task due to effects such as surface reconstruction, band bending, self-consistent electronic level corrections to molecular adsorbates, and the polarization of surface states by an applied electric field. All these effects influence STM measurements and data interpretation.[7,9–11] A detailed understanding of atomic contact properties is required as one pushes towards more exotic devices interfaced with silicon.[2,3,5]

STM height and current-voltage measurements on Si(100) have been reported extensively in literature for many years, include a broad range of hydrocarbons such as C_2H_4, C_2H_2, styrene, benzene, diphenyl, and cyclopentene.[2,5,6,12–18] In many cases a molecular sample appears only as a fraction of its geometric height above the substrate (in the STM image). In other instances the sample can even appear darker than the substrate[12,15] which can be misinterpreted to imply that the sample is located inside or even below the substrate. It is also not always clear what role is played by the applied bias in a STM measurement. These and other puzzles have led to many useful theoretical investigations of STM image height characteristics.

Most recently, Hückel based modeling of styrene on Si has been reported,[16] with an emphasis on lateral transport, heights, and methyl end groups. The bias dependence of styrene image heights and tip sample interaction have also been of interest, particularly with a lack of explanation for the negative heights arising at lower imaging voltages.[15] As well, height simulations of C_2H_2 and C_2H_4 contrast inversion have uncovered noticeable contributions due to surface polarization on clean Si(100).[7,14] Polarization by an applied electric field extends clean Si(100) dimer states into the vacuum to such an extent that their measured profile height lies above that of adsorbed C_2H_4 molecules under certain bias conditions. Smaller hydrocarbons such as C_2H_4 remain closely attached to the surface and are therefore only lightly affected by the applied bias. However, due to its small height, the molecule can appear smaller than nearby clean silicon dimers which undergo slight polarization under an applied electric field. This polarization raises the STM height profile of the clean substrate by approximately 0.5 Å[8] and is therefore an issue for short molecules but not so critical to interpreting the height features of longer molecules such as styrene. These effects are limited to clean silicon surfaces. Finally, the relative equilibrium energetic position of occupied surface states was shown to influence STM heights.[19] Due to the immense importance of interpreting STM height data, further investigations of STM image heights on Si(100) are warranted. In particular, we note that all previous atomistic studies of this problem were based on calculating the electronic structure of the tip and substrate *separately* and at equilibrium. On the other hand, when current flows from the STM tip into the substrate, the problem in inherently non-equilibrium and in principle the atomic potentials should be determined under non-equilibrium conditions. It is the purpose of this paper to carry out such a non-equilibrium calculation.

Our work is concerned with passivated Si(100). We

address three open questions regarding molecular STM height measurements on passivated Si(100): what is the role of electrostatics, what is the role of the substrate band gap, and is a non-equilibrium model required to obtain results that match experimental data? In this context we examine the experimentally well studied system of styrene adsorbed on hydrogen passivated Si(100). A subtle interplay between tip-sample electrostatics and surface band structure is shown to strongly influence STM height measurements. The importance of applying the self-consistent non-equilibrium Green's function (NEGF) method[20] under high bias is highlighted. As one of the longer hydrocarbons studied extensively on silicon, styrene resides close to the STM tip even at substantial bias voltages and low imaging currents (-3 V, 50 pA).[15] Under these STM imaging conditions styrene is subjected to a large voltage drop which shifts its energy levels thereby affecting its height characteristics. On the other hand, at low bias it is the Si-substrate band gap that dominates transmission. We are able to attribute the experimentally observed negative styrene STM heights at (-1.5 V, 50 pA)[15] to low transmission at the edges of the Si(100) band gap. Finally, we compare the NEGF results with that obtained by the Tersoff-Hamann approximation.[21–23]

The rest of the paper is organized into five subsequent sections. Section II discusses the geometry under investigation. Section III outlines the *ab-initio* NEGF method and other calculation details. Section IV presents current-voltage characteristics for styrene on Si(100)-(2x1). In section V the Tersoff-Hamann approximation is compared with the NEGF results. Section VI is reserved for a short summary.

II. ATOMIC GEOMETRY

We begin by discussing the atomic geometry for three tip-sample systems in our study. The first system is composed of an unrelaxed Al(100) tip above an Al(100) surface (Fig.1a). This system is used to qualitatively benchmark our STM model. The remaining two systems are hydrogen passivated Si(100) and styrene on Si(100) (Figs.1b and 1c) for which we seek a quantitative understanding of the styrene heights observed experimentally. The atomic structures are obtained by DFT total energy relaxation using the electronic package SIESTA.[24]

A. Si(100) substrate and STM geometry

To model the STM tip above hydrogen passivated Si(100) and styrene passivated Si(100), we have several considerations: tip-sample atomic structure, tip relaxation, positioning of the tip above the sample, and the potential profile through the tip-sample structure that is needed when calculating the tunneling current.

1. Tip and sample structure

To model a metal tip, we use an Al(100)-(3x3) structure with strained coordinates to ensure that the tip geometry embeds into the (7.65 Å x 7.65 Å) periodic Si(100)-(2x2) unit cell. The imposed strain on the natural Al(100)-(3x3) unit cell dimensions of (8.57 Å x 8.57 Å) turns out to have insignificant effect on the metallic tip density of states (DOS) and transmission coefficient, in contrast to covalent bonded systems where bulk properties can be significantly altered, and is therefore a fair approximation which we adopt. Above silicon a twenty three atom tip is placed: the first two bulk-like layers are frozen and the remaining five tip atoms are permitted to relax. Two bulk layers are sufficient to model the tip electronic structure, since tip surface states tend to dominate STM tip transmission coefficient.[25,26]

In experimental measurements[15] on styrene, the STM tip can be placed in direct contact with the molecule, hence tip-sample geometry relaxation is a key ingredient for obtaining a proper understanding of the measured data. Therefore, we relax the tip above the styrene molecule at each $I(z)$ point, where I is current and z the coordinate along the tip-sample direction. The z values are set at 1 Å intervals. All geometry optimizations are performed via the conjugate gradient method, using the local density approximation (LDA)[24] and are converged to 0.01 eV/Å on a real-space grid corresponding to energy cutoff of 300 Ryd.

Careful consideration is taken in the placement of the tip apex atom above the sample. A full image scan within our self-consistent non-equilibrium method (see below) would be too computationally intensive. Instead, the tip is placed above the point of largest LDOS of the sample and then retracted at a given voltage to build up a current versus distance $I(z)$ plot. In the case of styrene between 0 V and -3 V bias, the highest LDOS point is dominated by carbon-carbon π bonding,[7,15] hence the tip is placed above the highest carbon atom (see red dot in Fig.1c). Hydrogen passivated Si(100) results in symmetric dimers, so the tip may be placed above either hydrogen atom and an additional deeper Si atom (see red dots in Fig.1b).

For each of the three geometries in Fig.1, the tip is placed 2 Å above the point of interest: this point defines the $z = 0$ for subsequent $I(z)$ calculations when the tip is retracted to 10 Å. Due to this definition of $z = 0$, the 5.3 Å offset between $I(z)$ origins for H/Si(100) and styrene/Si(100) (Fig.1c) has to be taken into account when comparing $I(z)$ plots to extract the STM heights.

2. Two probe transport structure

Using the atomic coordinates obtained by total energy relaxation described above, we build a two-probe transport simulation of the tip-sample system for calculating the $I(z)$ curves. The two-probe system has a scattering region plus a top and a bottom lead. The scattering re-

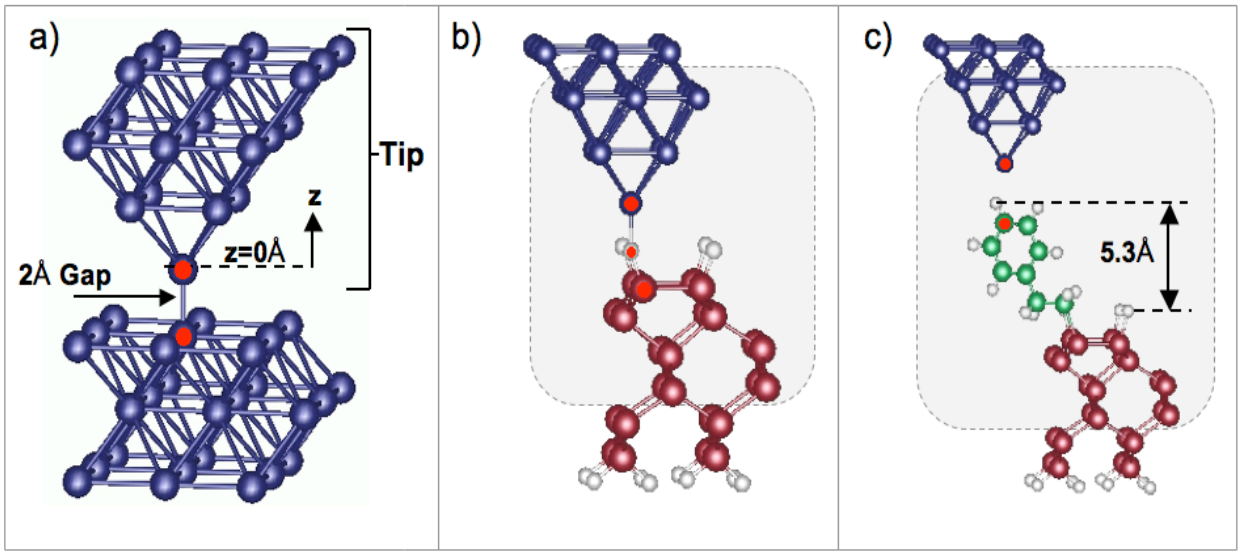

FIG. 1: Atomic geometry of the tip-sample system. The structures are obtained by DFT total energy relaxation. (a) Al(100)-(3x3) tip and Al substrate structure. The same tip is placed above all Si(100) substrates. (b) Al tip on Si(100)-(2x1) passivated and reconstructed surface. (c) Al tip on Si(100)-(2x1) styrene surface. To reduce computation, the styrene unit cell includes one styrene molecule from the relaxed geometry of an infinite (periodic) styrene surface. Within LDA, the optimized geometric height of styrene against a Si(100) passivated background is 5.3Å. The red dots indicate the position of free atomic orbitals used for $I(z)$ calculation (see section III C). The shaded gray area indicates the subset of atoms which form the scattering region of two-probe transport analysis by NEGF.

gion consists of the atoms in the shaded boxes of Fig.1b and 1c. Namely, a H/Si(100) or sytrene/Si(100) surface along with a 14 atom tip and four Si(100) layers, are included in the scattering region. The tip is connected to an Al lead that is modeled by perfect Al(100) crystal planes extending to $z = +\infty$. Similarly, the Si substrate in the scattering region is connected to a perfect Si(100) lead extending to $z = -\infty$. A voltage bias is applied across the the two leads which drives a current through the tip-sample two probe system.

B. Al(100) substrate and STM geometry

An Al(100) tip above an Al(100) substrate is taken as a benchmark of our $I(z)$ calculation (see Section III C). For this case the structure is relaxed at a tip-sample separation of 10 Å. No further relaxation is carried out for other values of z. A two probe tip-substrate system is formed by attaching Al(100) leads for both the tip and substrate. To calculate $I(z)$, the apex atom is placed directly above an aluminum surface atom and retracted (see Fig.1a and 3). The Al(100) tip-substrate system can be described by the natural Al(100)-(3x3) unit cell size of (8.57 Å x 8.57 Å), the scattering region of the two probe system includes five tip atoms and five bulk Al layers as shown in Fig.1a.

III. THEORETICAL METHOD

When a bias voltage is applied to a two probe transport structure to drive a current, the scattering region is in a non-equilibrium state. At present, real space density functional theory (DFT) carried out within the Keldysh non-equilibrium Green's function (NEGF) framework is the state-of-the-art technique[20,27,28] for analyzing non-equilibrium quantum transport in atomic systems. We make use of this technique and its associated electronic package Matdcal[20] to calculate $I(z)$ curves. The basic idea behind the NEGF-DFT formalism is to calculate the Hamiltonian of a two probe device system using DFT, determine the non-equilibrium quantum statistics of the transport problem using NEGF, and deal with electron the transport open boundary conditions using real space numerical techniques.[20,28] We briefly outline our simulation method in this section.

A. Transmission coefficient

Within NEGF, the transmission coefficient $T = T(E, V)$ is calculated via Green's functions, here E is the electron energy and V the bias voltage. Once the device Hamiltonian H is obtained by NEGF-DFT,[20,28] the retarded Green's function G of the device scattering

region at energy E is obtained as

$$G(E) = [(E + i\eta)S - H - \Sigma_S(E) - \Sigma_T(E)]^{-1} \quad (1)$$

where η is a small positive infinitesimal, S is the overlap matrix between atomic basis functions, and H the device Hamiltonian matrix. Quantities Σ_S and Σ_T are the self-energies of the substrate and STM tip, respectively. They are calculated via recursive Fourier methods.[29,30] The transmission coefficient of a two probe tip-sample system is determined by

$$T(E, V) = tr\left[\Gamma_S G \Gamma_T G^\dagger\right] \quad (2)$$

where $\Gamma_{S,T} = i(\Sigma_{S,T} - \Sigma^\dagger_{S,T})$ are the line-width functions describing coupling of the device scattering region with the device leads. The steady state current under a given bias is calculated as

$$I = \frac{q}{h}\int_{-\infty}^{\infty} T(E)[f_S(E) - f_T(E)]dE, \quad (3)$$

$$f_{S,T}(E) = \frac{1}{1 + e^{(E-\mu_{S,T})/k_B T}}, \quad (4)$$

where $f_{S,T}$ is the Fermi function of the substrate/tip with an electro-chemical potential of $\mu_{S,T}$. At low temperature, the integration limits reduces to the bias window, from μ_S to μ_T. To obtain an $I(z)$ plot, the transmission coefficient $T(E, V)$ and therefore the tip-sample Hamiltonian H must be calculated at many z points.

B. Two probe device Hamiltonian

In our STM simulation of the $I(z)$ curves, we divide the device Hamiltonian H into two parts: the equilibrium Hamiltonian $\hat{H}_0$ and the non-equilibrium Hartree potential profile $V_{\delta H}(\vec{r})$. The total non-equilibrium Hamiltonian is therefore given by $\hat{H} = \hat{H}_0 + V_{\delta H}(\vec{r})$. Here $\hat{H}_0$ represents the equilibrium Hamiltonian of the tip-sample system without bias, we calculate it within the electronic package SIESTA.[24] The second part of the Hamiltonian, $V_{\delta H}(\vec{r})$, represents Hartree potential profile between the STM tip and the sample under an a three-dimensional applied bias and during current flow, we calculate it via the NEGF-DFT package Matdcal[20]. We use the GGA exchange-correlation potential[31] in $\hat{H}_0$, which improves the Si band gap from 0.5eV by LDA[32] to 0.85eV.[33]

The non-equilibrium Hartree potential profile $V_{\delta H}(\vec{r})$ is obtained by solving the Poisson equation,

$$\nabla^2 V_{\delta H}(\vec{r}) = -4\pi\delta\rho(\vec{r}) \quad (5)$$

where $\delta\rho(\vec{r}) \equiv \rho_{bias}(\vec{r}) - \rho_{eq}(\vec{r})$, ρ_{bias} is the non-equilibrium charge density and ρ_{eq} the equilibrium charge density, both are obtained by calculating the non-equilibrium density matrix within the NEGF-DFT package Matdcal.[20]

The calculation of $\hat{H}_0$ is carried out with a 200 Ryd energy cutoff. The k-space reciprocal vector for each slab geometry is set at 20 Å.[24,34] We employ double zeta polarized (DZP) basis orbitals on hydrogen, carbon, and silicon. For aluminum a single zeta polarized (SZP) basis is applied to all atoms. The basis function for the tip apex atom and the surface atom just below the tip will be discussed in the next subsection (see red dots in Fig.1a). The calculation of $V_{\delta H}(\vec{r})$ within Matdcal[20] in the two probe tip-sample geometry is carried out on a three-dimensional real space mesh where mesh size corresponds to a 150 Ryd energy cutoff. Sixteen k-points are required to converge the two-dimensional Brillouin zone sampling in the x-y direction (transport in z-direction). To reduce computational time in the two probe NEGF analysis at finite bias, a single zeta (SZ) basis set is utilized in Matdcal.[20,35] The NEGF-DFT analysis of Matdcal[20] provides potential drop between a tip and substrate within the fully self-consistent framework at different tip-sample distances and bias voltages. Further details of the NEGF-DFT implementation can be found in Refs.[20,28].

C. Basis set

For a two probe tip-sample system, the value of tunneling current $I(z)$ is sensitive to wave-function overlap between the surface and tip across the vacuum in between. This becomes a technical issue when strongly localized LCAO basis set[24] is used in the DFT analysis. It is reasonable to assume that the atom at the tip apex and atoms at the surface have the same character of wave function decay into vacuum as that of a free isolated atom: these wave functions are valance electron eigenfunctions of isolated atoms having a long tail decaying into vacuum. In our calculations, we assign these free atomic orbitals as basis functions for the tip apex atom and atoms at the surface beneath the tip. Practically, we generate free atomic orbitals following the approach of Ref.[36], using a large radial cutoff of 15 Bohr. The secondary split-off orbitals[24,36] are defined at 5 Bohr as are polarization orbitals. These parameters are the same for all free atomic orbitals implemented in this work with results comparable to an earlier publication.[39]

The free atomic orbitals introduce some error into the eigenstates and the total energy. To minimize this error, no more than two or three free atomic orbitals are assigned to any given unit cell (see Fig.1): one for the tip apex atom and a second or third (if necessary) for the sample atoms beneath the tip – no more is required as these atoms dominate the $I(z)$ characteristics. Fig.2 displays the effect of introducing free atomic orbitals to the Si(100)-(2x2) surface atoms highlighted by red dots of Fig.1, against reference calculations employing optimized DZP basis sets without any free orbitals. The projected density of states (PDOS) plots are extracted from isolated H/Si(100) and styrene/Si(100) slabs shown in Fig.1. For H/Si(100) the PDOS shift is about 0.1eV; for styrene it is about 0.25eV. With a free atomic orbital

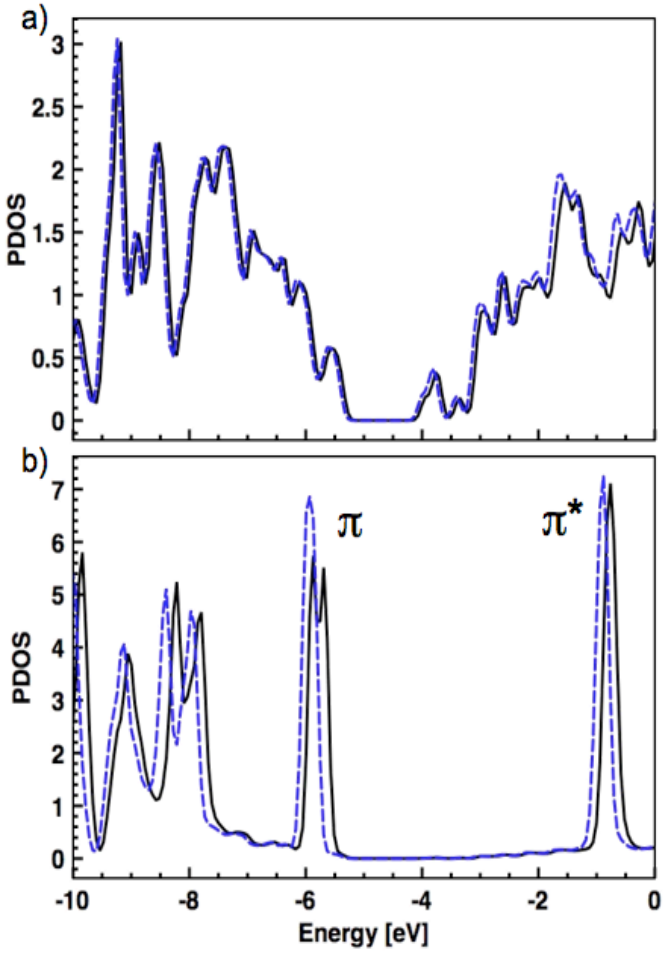

FIG. 2: PDOS for the Si(100)-(2x2) unit cell. Dashed blue line: calculated with free atomic orbitals placed as shown by the red dots in Fig.1. Solid black line: calculated without the free orbitals. (a) For the first layer of silicon atoms and hydrogens on H-passivated Si(100). (b) For styrene on Si(100). The agreement is reasonable with or without the free atomic orbitals. Similar agreement (not shown) is found for the case of Al(100) substrate.

the styrene system has a total energy of -4155.85 eV, to be compared to -4155.67 eV when free orbital is absent. With free orbitals the H/Si(100) system has a total energy of -2778.71 eV, to be compared with -2778.94 eV without it. These are very small differences indicating that the use of a few free atomic orbitals only introduces an insignificant error for the purposes of our investigation. In subsequent simulations, we use free atomic orbitals on the tip apex atom and the substrate atoms of interest.

We find that the above procedure succeeds well in modeling STM current decay, as shown in Fig.3 where a qualitative match to experimental decay is achieved. Here, the $I(z)$ curve is calculated for an Al(100) tip and an Al(100) substrate biased at $V = 50$meV (solid line). For such a very small bias we have safely neglected the non-equilibrium potential $V_{\delta H}(\vec{r})$ of Eq.(5) in the transmission calculation. Compare this to the $I(z)$ curve obtained without using free atomic orbitals (dashed line), it decays much faster in an unphysical manner.

To have a more concrete understanding, in Fig.3 we also plot experimental data in the same range of z from Ref.[38], where the tip is tungsten and substrate is Au(111)-(22x$\sqrt{3}$). The work functions of Au and W are[40] -5.31 eV and -4.45 eV respectively, and for Al(100) it is -4.2 eV. These values can be used in a simple square barrier STM model[41] to estimate how much difference we expect in current decay for the Al/Al system (our theory) and for the W/Au system (experiment). In square barrier model,[40] the current decays exponentially in z,

$$I = I_0 e^{-1.025\sqrt{\phi}z}, \tag{6}$$

where z is in units of angstrom, ϕ is the work function in units of eV, and I_0 is assumed to be the same for both systems. From Eq.(6), we find that the $I(z)$ decay expected from the experimental system should not exceed that of the simulated Al(100) geometry by more than ~ 0.11 dec/Å, assuming an experimental work function of -5.31 eV. Indeed, the theoretical result (solid line) in Fig.3 shows a decay rate close to that of the experimental data (a qualitative difference of 0.11 dec/Å is within the bounds of experimental error), indicating that the procedure of using free atomic orbitals is appropriate. Finally, the mismatch between experimental data and the theoretical solid line in Fig.3 below 3.5Å is likely due to structure relaxation which we have neglected for the Al-on-Al simulation (as mentioned above, for this system the relaxed structure at z =10 Åis used for all other z values). At $z = 0$ (tip-sample distance at 2 Å), the difference between theory and experimental data is about 10%, suggesting relaxation effects to play a role for small z values. In addition, the collapse of the vacuum barrier at small z may also differ for W-on-Au and Al-on-Al systems.

IV. STYRENE IMAGE HEIGHTS ON SI(100)

Using the theoretical technique discussed in section III, we have calculated the STM image height of styrene on hydrogen passivated Si(100). Three bias voltages at 50 pA current are examined in detail: -3 V where the π state is fully conducting, -2 V where the π state begins to conduct, and -1.2 V where height inversion is observed.[2,15,16] We quantitatively analyze the role of the non-equilibrium potential profile $V_{\delta H}(\vec{r})$ and the band gap in determining STM heights.

As mentioned above, for atoms just across the vacuum gap we assign free orbitals. Specifically, we assign a free atomic orbital to the apex atom of the Al(100) tip (see apex red dot in Fig.1). For hydrogen passivated Si(100), DZP free atomic orbitals are placed sparingly on one Si-H surface pair in the simulated (2x2) unit cell (Fig.1c).

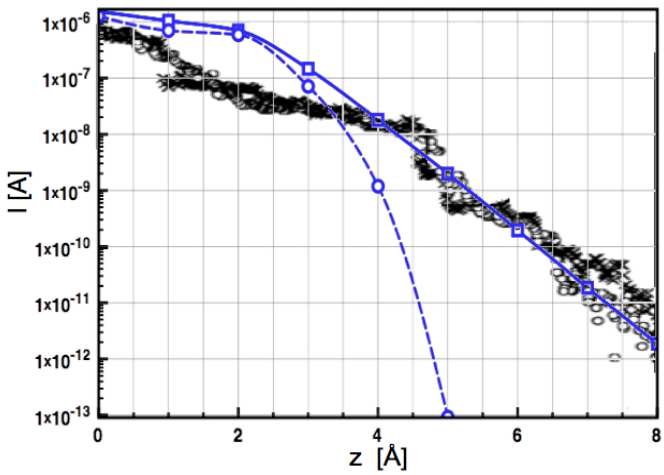

FIG. 3: $I = I(z)$ versus z for Al tip on Al(100) at 50 meV bias for E_f=-4 eV. Solid line: using free atomic orbitals. Dashed line: using SZP with 7 Bohr cutoff. Symbols x are experimental data reprinted with permission from Ref.[38]. The offset for the experimental data is -0.8 Å from the origin provided in Ref.[38] since the nearest neighbor distance of Al is 2.86 Å and the above $I(z)$, as with all plots in this paper, sets its origin at a 2 Å atomic separation.

Because occupied surface states involve strong hybridization between the hydrogen and silicon atoms, free atomic orbitals are placed on two atoms (red dots in Fig.1c). On the other hand, the conducting π state of styrene centered at -6 eV (see (Fig.2b) is much more weakly hybridized, as well the π state is composed of carbon-carbon bonding.[15] Thus, a single free atomic orbital is placed on the highest carbon atom over which the tip is positioned (see red dot in Fig.1c).

A. Styrene at -3.0V: full π state conduction

Simulated and experimental heights match well for styrene biased at -3 V and 50 pA (see Fig.4a). The experimentally measured styrene height is approximately 3.3 Å at 60 pA.[2,16] Our calculation gives 3.4 Å at 50 pA which is in good agreement. This 3.4 Å result is obtained as follows. The $I = 50$ pA line (horizontal dot-dashed line) in Fig.4a cuts the two $I(z)$ curves (solid lines) at $z_H = 6.4$ Å for H/Si, and at $z_{styrene} = 4.5$ Å for styrene. From geometries in Fig.1b,c, the apparent height of styrene at 50 pA is obtained by subtracting the difference $z_H - z_{styrene} = 1.9$ Å from the 5.3 Å offset between the $z = 0$ points in Fig.1b and 1c. We therefore obtain 3.4 Å for the styrene height at (-3 V, 50 pA). The two solid $I(z)$ curves in Fig.4 a further suggest that raising the set current from 50 pA to 60 pA, changes the styrene height measurement very insignificantly. The agreement between theory and experiment height values at (-3 V, 50 pA) is, indeed, remarkable. It is also worth noting that the $I(z)$ current decay of approximately 1 dec/Å over both H/Si(100) and styrene is consistent with experimental measurements over cyclopentene passivated Si(100).[42]

The small height difference of ~ 0.1Å between our calculation and experimental data[16] is likely due to subtle polarization effects, or due to the approximation of using free atomic orbitals. There have been some disagreement in styrene heights on hydrogen passivated Si(100) at -3 V in literature, including 2.8 Å[15] and 3.3 Å,[2,16] which could be due to a slight variation in the point over which height measurements were taken. More recently, it has been observed that measurements at (-3.0 V, 50 pA) to the side of carbon ring gave a reduced height of 3.1 Å.[16] In our results reported here, all $I(z)$ curves are calculated by placing the tip apex just above the highest carbon atom on the carbon ring.

In Fig.4a, the two dashed $I(z)$ curves were obtained without the non-equilibrium potential profile $V_{\delta H}(\vec{r})$ of Eq.(5), namely they are calculated at equilibrium. For both styrene and H/Si, $V_{\delta H}(\vec{r})$ increases the tunneling current. Using these dashed $I(z)$ curves, we still obtain a similar styrene height as the full non-equilibrium calculation (differs by only 0.2Å). Therefore at -3 V, the main role of the non-equilibrium potential $V_{\delta H}(\vec{r})$ is to lower the vacuum barrier and increase the current (compare dashed and solid lines in Fig.4a). In particular, due to $V_{\delta H}(\vec{r})$, the styrene tip-sample distance increases by ~ 0.5 Å at (-3 V, 50 pA), compared with that obtained with the equilibrium Hamiltonian. For tunneling into H/Si, there is a similar although slightly larger increase in current when $V_{\delta H}(\vec{r})$ is included, see Fig.4a.

For a given bias $V = \mu_S - \mu_T$, current is contributed by states within the bias window $\mu_S - \mu_T$ by Eq.(4). Tunneling into styrene is largely mediated by the molecular π-state, therefore it is important if the π-state is within this bias window or not. In our calculations, μ_S is set at the Fermi level of the n^{++} doped Si contacts, namely at -3.9 eV,[43] and μ_T is shifted by the applied bias voltage. Fig.4b plots transmission coefficients $T(E)$ at -3 V bias when the tip apex is at 2 Åaway from the highest atom on the sample (defined as $z = 0$, see last paragraph of Section II A 1), $\mu_{S,T}$ are indicated by the arrows. Fig.4b shows that the π-state of styrene is outside the bias window and in contrast, $T(E)$ for tunneling into H/Si has broad peak inside the bias window. On the other hand, for $z = 4$ Å (the tip apex is at 6Åfrom the styrene molecule), the styrene π-state is within the bias window of -3 V, as shown by the solid curve in Fig.5. Importantly, π-state is within the bias window whether or not the non-equilibrium potential $V_{\delta H}(\vec{r})$ is included in our calculation. This explains why the styrene height at (-3 V, 50 pA) can be rather well obtained using only the equilibrium Hamiltonian without $V_{\delta H}(\vec{r})$. In the next subsection, we show that the height behavior becomes very different depending on $V_{\delta H}(\vec{r})$.

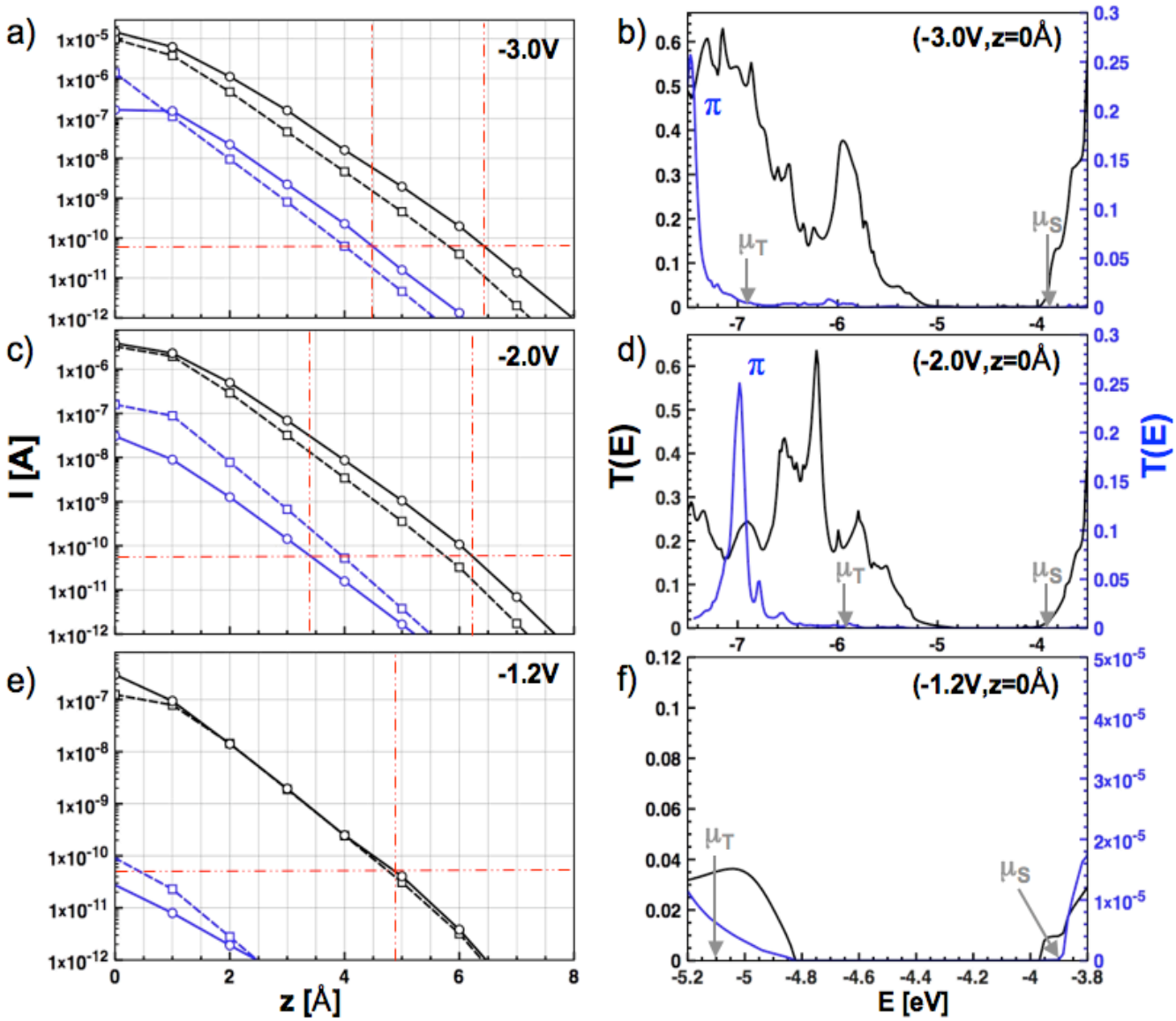

FIG. 4: (color online) $I(z)$ characteristics for H/Si(100) in black (equilibrium dashed and non-equilibrium solid) and styrene in blue at: a) -3 V bias, c) -2 V bias, and e) -1.2 V bias. The experimental current value of 50 pA is marked by dashed red lines. Equilibrium $I(z)$ results are obtained by calculating the transmission between both electro-chemical potentials without including a potential drop in the device region, whereas non-equilibrium results include the self-consistent potential profile $V_{\delta H}(\vec{r})$. Non-equilibrium transmission plots may be found adjacent to each $I(z)$ figure with H/Si(100) in black and styrene in blue: b) -3 V, z=0 Å, η=10 meV; d) -2 V, z=0 Å, η=10 meV; f) -1.5 V, z=0 Å, η=1 μeV. Recall, η is defined in equation (1) as a broadening constant for the retarded Green's function of the device. Again, each $I(z)$ curve has its origin set at 2 Å above the atom of interest marked in Figure 1 and relaxation is included in the styrene $I(z)$ plots. The π state for styrene is marked in the transmission plots as are the electrochemical potentials μ_T and μ_S, respectively.

B. Styrene at -2.0V: lowering the conducting π state

$I(z)$ curves for (-2 V, 50 pA) are plotted in Fig.4c. Here, for tunneling into H/Si the non-equilibrium potential $V_{\delta H}(\vec{r})$ still increases current $I(z)$ as at -3 V. However, for styrene the behavior is reversed: $V_{\delta H}(\vec{r})$ decreases the current. The reason for this decrease can be seen in Fig.5: the styrene π-state (dashed line) is now outside the bias window between $\mu_S = -3.9$eV and $\mu_T = (\mu_S - 2eV) = -5.9$ eV due to $V_{\delta H}(\vec{r})$. It is however inside the window without $V_{\delta H}(\vec{r})$ (dotted line). Pulling the π-state to outside the bias window by $V_{\delta H}(\vec{r})$ results in a net decrease of 0.6 Å between the equilibrium and non-equilibrium results at 50 pA. The total height correction due to $V_{\delta H}(\vec{r})$ over both styrene and H/Si(100) is about 1 Å. Therefore, using the method for height calculation described at the beginning of Section IV A, from

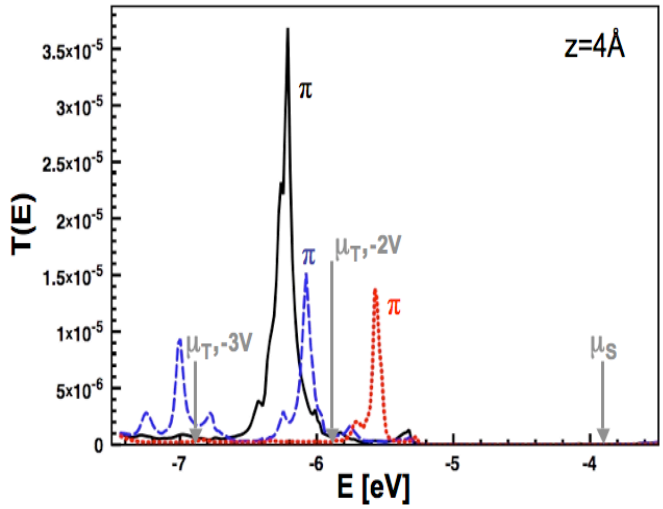

FIG. 5: (color online) Transmission coefficient $T(E)$ versus electron energy E at $z = 4$ Å in Fig.4 for styrene biased at -3 V (solid black line); and -2 V (dashed blue line). Non-equilibrium potential drop $V_{\delta H}(\vec{r})$ is included when obtaining these curves. The dotted red line is $T(E)$ without $V_{\delta H}(\vec{r})$. The peaks in $T(E)$ are due to the molecular π-state of styrene. At -3 V bias, the π-state is within the bias window indicated by arrows of $\mu_{S,T}$. At -2 V bias, it is outside the bias window due to the non-equilibrium potential drop $V_{\delta H}(\vec{r})$. The peak of $T(E)$ at -3 V is much larger than that at -2 V due to a decrease in the vacuum barrier under a larger bias.

the two $I(z)$ curves (solid lines) in Fig.4c we obtain a styrene height of 2.5 Å for (-2 V, 50 pA). This is to be compared with the experimental value of 2.6 Å at (-2 V, 60 pA)[2,16]. Again, we compare results against experimental styrene heights away from the ends of an adsorbed chain, and the agreement is very good. Importantly, the effect of $V_{\delta H}(\vec{r})$ is very important at -2 V: it places the STM tip closer to the styrene than would be estimated using the equilibrium Hamiltonian. Again, due to a reduction of the vacuum barrier, we note an increase in the H/Si(100) tip-sample distance of approximately 0.6 Å over that predicted by the equilibrium Hamiltonian. Finally, Fig.4d plots $T(E)$ at $z = 0$ and qualitative features are similar to that of Fig.4b.

C. Styrene at -1.2V: the height inversion

Figs.4e plots $I(z)$ curves for (-1.2 V, 50 pA) showing a styrene height inversion, *i.e.* styrene (almost) appears lower than H/Si(100). This is consistent with the experimental trend of height inversion observed at (-1.5 V, 50 pA).[15] The difference of -0.3 V bias may be attributed to an underestimation of the Si band gap in our DFT calculations: our DFT-GGA calculation gives[31] a gap of 0.85eV while the experimental gap is 1.15eV. Therefore, the height inversion at -1.2 V obtained from our model compares well with the experimental observation of height inversion at -1.5 V.

Contrary to expectations, we find that tip-sample bonding interaction is *not* responsible for the observed styrene height inversion. This is because, at lower bias voltages, it is the band gap which determines STM transmission characteristics. Fig.4f demonstrates this feature: at -1.2 V bias the main part of the $T(E)$ spectra falls within the Si band gap thus not contributing to conduction, leaving only a small surface DOS at the edges of the band gap to contribute. This leads to a drastic reduction in current flow through styrene at this bias, resulting in the observed height inversion.

Quantitatively, for (-1.5 V, 50 pA) the experimental height is reported to be ~ -0.25 Å.[15] Using the height calculation method described at the beginning of Section IV A, our theory gives 0.1 Å at (-1.2 V, 50 pA). Therefore, although the theoretical height is drastically reduced which mimics the qualitative feature of heigh inversion of the measurement, it does not quantitatively capture the experimental inversion value with a small error about 0.25 Å. The source of this error is unlikely to be related to the geometry because it was carefully relaxed for each value of z. We hypothesize that the error is due to the details of DFT: the conduction and valance band curvatures are reflected in the surface LDOS which contributes to conduction, with lower curvature resulting in a larger surface LDOS and vice versa.[11] This curvature depends on the DFT basis set. Nevertheless, qualitatively and even semi-quantitatively, our theory reproduces the height inversion feature of the experimental data.

D. Bonding distance

Now let's return to the question of a bonding contact between an atomic sample and a STM tip as posed in the introduction. There are two main physical effects which limit the full current at full contact $z = 0$: the resistance of the molecule and the Si(100) band gap. The molecule impedes conduction from bulk Si(100) states and lowers the current by approximately two orders of magnitude at -3 V and at -2 V, as shown in Fig.4a and 4b at $z = 0$. Notably, at full contact the styrene π-state is pulled out of the bias window even at -3 V bias (see Fig.4b), hence the observed insulating type of resistance. At full contact, if a level lines-up between the chemical potentials $\mu_{S,T}$, conductance will be high, otherwise the molecule conducts poorly. At -1.2 V, the low LDOS of styrene in the bias window together with the Si(100) band gap affect conduction such that current is four orders of magnitude smaller than that on H/Si(100). Our observation is that an Al tip placed at 2 Å bonding distance ($z = 0$) above either H/Si(100) or a styrene molecule forms a physisorption bond. This is confirmed by a charge density plot of the tip-sample interface. Thus, the lack of a strong chemical bond between styrene and the STM tip does not play a role in the observed decrease

from H/Si(100) conduction to styrene conduction – since the tip also forms a weak physisorption bond with the H/Si(100) surface. Further investigation into chemical bonding versus physisorption bonding conduction characteristics is left to future work and other metallic tips such as tungsten should be investigated. However, here it has been shown even current at full contact depends strongly on the presence of a bulk band gap and the conducting resonance properties of the molecule, and may vary significantly with only a small change in bias (*i.e.* -1.2 V to -2 V). Our full self-consistent NEGF-DFT theory presented here captures these complicated effects.

E. Si(100) Band Bending

Silicon band bending[44] is another important issue which has not been considered so far. For our problem studied here, it is found to have little effect on transmission: it only provides a maximum shift of surface states about 0.1 eV at room temperature and negative STM bias,[43] for n-type doping on the order of 10^{18} cm^{-3}. Band bending could shift surface states by 0.01-0.1eV without altering the qualitative features presented above. That is, the characteristics seen at -3V would be better matched to experimental results at -3.1V, *etc.* Even n-type doping on the order of 10^{16} cm^{-3} would only result in a 0.2 eV shift of surface states at room temperature. A proper treatment of banding bending within a true ab-initio methodology is beyond the scope of this work.[45] As a final remark, in this analysis we have excluded effects of electric field polarization, since strong polarization is so far known to be limited to clean silicon[7,8] whereas this work is focused on H-passivated Si(100).

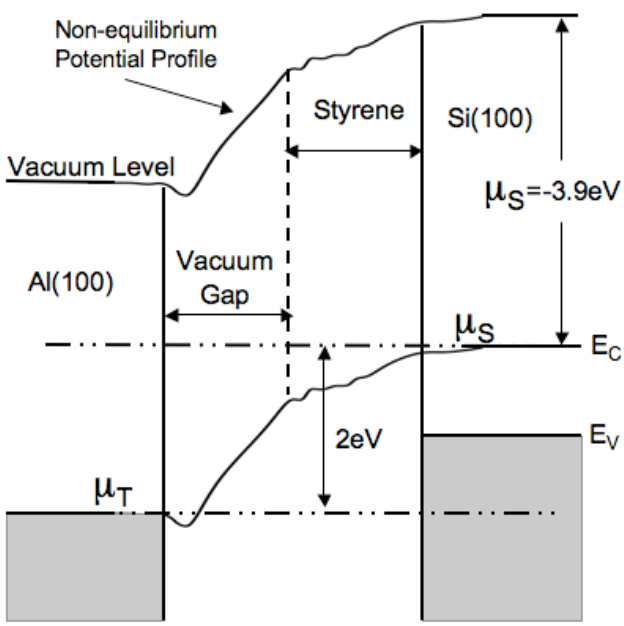

FIG. 6: Calculated non-equilibrium potential profile at -2 V bias for a styrene molecule situated between a grounded tip and Si(100) substrate (see Fig.1). The potential profile shown is taken as a z-direction cut directly through the atomic center of the tip apex. The Si(100) electrochemical potential μ_S is set at -3.9 eV, corresponding to a highly n-doped substrate and with the reference vacuum potential set at 0 eV. Under a -2 V bias the tip electrochemical potential $\mu_T = \mu_S - 2$ eV $= -5.9$ eV. Most of the potential drops across the vacuum region, with roughly one-third of the potential dropping across the styrene molecule – a ratio which depends on the size of the vacuum region. Similar results can be obtained via a simple capacitive model.[9]

V. COMPARISON TO TERSOFF-HAMANN APPROXIMATION

So far our results are obtained from the self-consistent NEGF theory as discussed in Section III. For comparison, in the following we calculate the STM heights by the Tersoff-Hamann (T-H) approximation.[22,23] We begin by manipulating Eq.(2) as follows:

$$\begin{aligned} T &= tr[\Gamma_S G \Gamma_T G^\dagger] \\ &= tr[\tau_S A_S \tau_S^\dagger G \tau_T^\dagger A_T \tau_T G^\dagger] \\ &= tr[A_S \tau_S^\dagger G \tau_T^\dagger A_T \tau_T G^\dagger \tau_S] \\ &= tr[A_S M A_T M^\dagger] \end{aligned} \tag{7}$$

where G is the Green's function of the scattering region, τ_S and τ_T are couplings of this region to the semi-infinite substrate and tip, M represents coupling between the left and right contact spectral functions A_T and A_S[27], where $A_{S,T} = G\Gamma_{S,T}G^\dagger$. If the coupling is weak we may take M to be a constant. If DOS in the metallic STM tip is relatively flat such that A_T may be approximated by a constant, one obtains approximate transmission coefficient, namely the T-H approximation:

$$T(E, \vec{r_0}) \propto tr[A_S(E, \vec{r_0})] = \rho_S(E, \vec{r_0}). \tag{8}$$

Therefore, in T-H approximation the tunneling current is determined by LDOS $\rho_S(E, \vec{r_0})$ of the sample at the tip apex position $\vec{r_0}$. The approximation involved in arriving at Eq.(8) dictates that T-H approximation is valid for STM height simulations in the strongly tunneling limit and it breaks down when tip-sample interactions are important. The larger the distance between the tip and sample, the better the T-H approximation.

In practical calculations using Eq.(8), electronic structures of the tip and sample are taken to be independent with each other and any tip-sample interaction is neglected. We chose to compute image heights at -3 V, because amongst the three voltages analyzed in Section IV, this case presents the largest distance between styrene and the tip at 50 pA. Fig.7 shows a height scan obtained by the T-H method at (-3 V, 50 pA) where separation between the highest styrene atom and the tip apex is

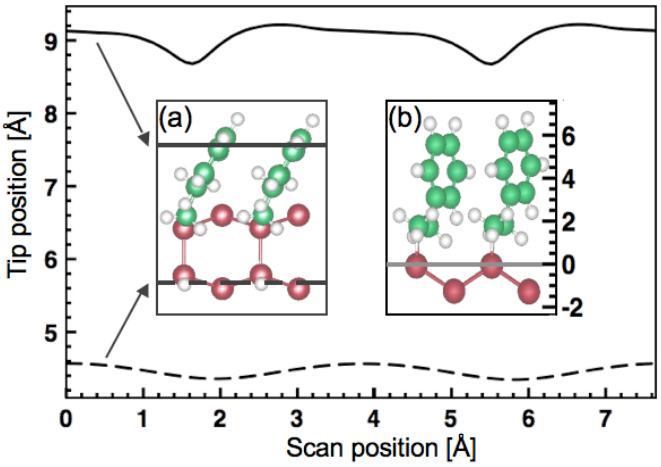

FIG. 7: STM height scan at (-3 V, 50 pA) calculated within the Tersoff-Hamann approximation. The data is extracted from the bias window of $\mu_S = -3.9$ eV to $\mu_T = \mu_S - 3$ eV $= -6.9$ eV at a constant electron density contour of 10^{-5} e/Bohr^3. Dashed line: taken over the maximum height of H-passivated Si(100) surface. Solid line: taken over the maximum height of a styrene chain where the π-state is clearly indicated by the two large dips in the curve. The height difference is 4.5 Å, which is about 1Å greater than that obtained by NEGF theory. Inset (a): showing orientation and position of the styrene and hydrogen Si(100) LDOS scans looking down on the Si(100) surface. Inset (b): a side view showing the origin of the tip position relative to the molecular heights. Note that the origin assigned here is unrelated to those taken in the $I(z)$ plots in the other figures.

6.5 Å. To have consistency when comparing the T-H approximation to the NEGF result of Section IV, we have maintained the same placement of free atomic orbitals shown in Fig. 1 and other DFT details. We find that the STM styrene height obtained by T-H method differs from the experimental value by about 1.0 Å (this has been independently confirmed in an Abinit[46] plane wave T-H calculation). This large difference is unlikely due to effects of the applied tip-sample electric field, because in for (-3 V, 50 pA), NEGF results in Section IV A showed that there is little difference in the calculated equilibrium and non-equilibrium styrene heights (they differ by only 0.2 Å, see Fig.4a and discussions in Section IV A). Therefore we attribute this difference to the electronic coupling between the tip and sample which has been neglected in the T-H approximation.

VI. SUMMARY

We have calculated the STM image heights of styrene on Si(100) using density functional theory (DFT) within the Keldysh non-equilibrium Green's function (NEGF) formalism. The non-equilibrium potential drop between Si(100) and a STM tip is determined self-consistently, and is found to play an important role in the calculated image heights. The non-equilibrium potential profile affects STM heights by shifting resonant molecular levels out of the bias window and by lowering the vacuum barrier. The presence of a bulk Si band gap is found to play a crucial role in observed molecular height inversion at low imaging voltages. Our NEGF formalism correctly and quantitatively captures STM heights of styrene on Si(100) as compared to experimental data. Our numerical results also provide a microscopic physical picture behind the height characteristics including the height inversion. We also present a comparison between results obtained by the NEGF-DFT formalism and the Tersoff-Hamann approximation, showing that non-equilibrium analysis can be important in the study of STM image heights of molecules.

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