

Adsorption of benzene on Si(100)-(2×1): Adsorption energies and STM image analysis by *ab initio* methods

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We model the adsorption and STM imaging of benzene on Si(100) by using first principles density functional methods and a perturbation approach for the tunneling current. The simulations are well in accordance with experimental data and reproduce the adsorption energies and the energy differences between adsorption sites remarkably well. We were able to simulate images and line scans of the two principal adsorption geometries and to show that they reproduce the actual measurements. The chemical nature of the tip in measurements is discussed and it is shown that a tip structure protruding several layers from the crystal face and terminated by a tungsten atom gives the best agreement with measurements. The results confirm the view that tunneling is dominated by a single tip atom.

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I. CHARACTERIZATION OF NANOSTRUCTURES

In recent years the adsorption of organic molecules on semiconductor surfaces has developed into one of the key fields in semiconductor research. The reason for it is simple. If the transport properties of these molecules are understood, or the exact way in which an electron propagates through them is understood, then the building of surface structures with exactly defined electronic properties is within reach of technical applications. However, the best candidate molecule for modeling of these nanostructure devices has not yet been identified. The reason for this is also obvious. Organic molecules possess an enormous variety of structures and, consequently, properties.

Experimentally, the preferred technique to study adsorbed molecules is the scanning tunneling microscope (STM). In topographic mode the real space images of carbon or silicon surfaces covered with single adsorbed molecules are often quite close to a chemist's intuition. In these cases the shape of the adsorbed molecule seemingly determines the structure observed by an STM. However, combined experimental and theoretical studies reveal a rather complex interplay between the STM tip and the electronic structure of substrate and adsorbate. In some detail, these studies have been accomplished for ethylene (C₂H₄),¹⁻⁴ acetylene (C₂H₂),^{1,5} and benzene (C₆H₆).^{6,7} Experimental studies exist for a number of alkenes.⁸⁻¹⁰

From a theoretical point of view STM imaging, although extensively researched and in principle understood, is still somewhat limited by the fact that most methods either are not fully *ab initio*¹¹⁻¹³ or do not yield quantitative predictions in all cases.^{2,3} Due to limited computer resources a combined treatment of sample and tip from first principles will remain a mere possibility for still some time. Although ample evidence exists for the influence of electric fields^{2,14} and the geometry¹⁵ or electronic structure¹⁶ of the tip, these cases usually pertain to single systems. An overall scheme quantifying different influences is still missing.

The present study of benzene C₆H₆ on Si(100)-(2×1) is a combined theoretical and experimental effort. Theoretically, the emphasis will be on quantitative descriptions of adsorption energies, tunnel currents, constant current contours, and absolute changes compared to the clean Si(100)-(2×1) dimer surface. We compare the results to previous simulations based on Hartree-Fock and density functional methods,¹⁰ and we show that the differences are only minor. Given the about ten times lower computational effort of these calculations, the deviation from the present plane wave computations are in a reasonable range.

II. THEORETICAL METHOD

The calculations were performed in two steps. We used first principles density functional theory (DFT) methods to calculate the electronic structure of the fully relaxed silicon surface with or without an adsorbed benzene molecule. The same method was employed to calculate the relaxation of a tungsten (100) surface with a single W apex atom.¹⁶ For the calculation of the tip wave functions we used the full potential augmented plane wave method¹⁷ (FLAPW). The results of these calculations provided the input for our integration scheme, where we computed the Bardeen integral of sample and tip states^{18,19} for a three-dimensional grid of tip positions above the sample surface.

The DFT method used for relaxations and electronic structure of the sample was the Vienna *ab initio* simulation package^{20,21} (VASP). The ultrasoft pseudopotentials were of the Vanderbilt type.²² Exchange correlations were described by the generalized gradient approach (GGA) of Perdew *et al.*²³ (PW91). The Brillouin zone of the silicon surface was sampled by eight *k* points of a Monkhorst grid. The energy cutoff in all calculations was about 300 eV. Forces on single atoms in the final iterations were less than 0.01 eV/Å. The same convergence criterion was employed for tip relaxations. In FLAPW computations we used ten *k*

points in the irreducible wedge in our convergence cycles. The wave functions of the tip were computed in a final loop confined to the $\bar{\Gamma}$ point. The reduction to only one point was necessary due to the large energy interval in the current calculations. As corrugations of the adsorbed molecules proved to be comparable to the layer spacing of the tungsten lattice, we modified the tungsten terminated tip accordingly. In the final simulations we used a pyramid of four layers, terminated by a single tungsten atom, to mimic the structure of a “sharp” tungsten tip. Details of tip calculations can be found in Ref. 19.

We calculated two substrate films: for the clean Si(100) surface we computed relaxations and electronic structures of an eight layer (2×1) surface. The Si atoms of the bottom surface were passivated with hydrogen. The same geometry was employed in the calculations of C_6H_6 in a two-bond configuration. Initially, this setup remained unchanged for our simulations of the four-bonded adsorption of benzene. The calculations revealed in this case, that the constraints of the setup—no free dimer between adsorption sites—lead to artificial ground state properties. Additional calculations therefore were necessary, simulating a row of four dimers in our unit cell. For computational efficiency these calculations were performed with a reduced number of four layers. Since, however, the relaxations of silicon subsurface atoms are a major source of the energy changes in adsorption processes, the bottom layer was in this case frozen to its position obtained with the full number of layers.

The error of the distance scales and the current values in the STM simulations is hard to quantify. Apart from errors due to the use of perturbation theory, which should not be significant given the high separation (5–9 Å) of tip and sample, the error due to numerical integration is about 20%.²⁴ This is the error of the absolute current values; the error in the relative values, which are the basis for the calculations of vertical distances and corrugation differences, is much lower. We expect the given distance values to be accurate to about 0.2 to 0.3 Å over the whole distance range from 5 to 9 Å (core-core distance).

III. Si(100)-(2×1)

The experimental and theoretical investigation of the clean Si(100) surface is one of the most captivating stories in surface science. The unsaturated Si bonds of surface atoms very early suggested a ground state (2×1) surface terminated by Si dimers. This reconstruction was eventually confirmed by theoretical and experimental investigations. However, the ensuing controversy due to photoemission data (suggesting buckled dimers²⁵) and STM measurements (suggesting symmetric dimers²⁶) remained. Only the advance of the variable temperature STM could finally establish that the ground state of the surface consists of buckled dimers.²⁷ Theoretical investigations with pseudopotential and full-potential methods supported this view.^{28,29} Currently, it is accepted that buckled dimers at room temperature change their buckling angle in a flip-flop motion³⁰ with a frequency well beyond the time resolution of an STM.

In order to determine the properties of adsorbed mol-

ecules on a Si(100) surface we first calculated the ground state properties of the clean Si(100) surface. As an accurate determination of relaxations requires the use of the theoretical rather than the experimental lattice, we initially determined the equilibrium lattice constant by minimizing the energy of a two-atom Si bulk cell. It is quite typical for the comparison of GGA and local density approximation (LDA) calculations that the GGA underestimates and the LDA overestimates the strength of chemical bonds: in the case of silicon the experimental lattice constant (5.43 Å) is between our GGA minimum (5.46 Å) and the LDA (5.40 Å) minimum value. Subsequent simulations were done with the GGA and the theoretical lattice of 5.46 Å.

We obtain a (2×1) buckled surface as the ground state of the clean silicon surface. The buckling angle is about 19° and the bond length of Si-Si bonds in a dimer is 2.2 Å. The energy gain of the buckled surface compared to an unbuckled one is 81 meV; the buckling angle as well as the energy gain corresponds to results obtained by full-potential linear muffin-tin orbital (LMTO) methods.²⁹ Similar results were obtained by Ness *et al.* using the projector augmented waves (PAW) method.²

It is not yet clear whether or how the flip-flop motion of the dimers and the tunneling process of single electron from the silicon surface to the STM tip are related. In a consistent theoretical model the problem would require a complicated dynamical analysis of electron scattering including surface-surface and surface-tip interactions. Since such a complete picture is still beyond our theoretical means, at least from the viewpoint of first principles computations, we mimic the Si(100)-(2×1) surface by silicon dimers with a constrained z coordinate of surface atoms. To estimate the validity of this setup we performed simulations of STM scans due to the electronic structure of the surface alone. Figure 1 displays the results of these simulations. The contour of the surface local density of states (LDOS), 10^{-8} states/eV, is displayed for the buckled surface the constrained surface, and two cases, where we mimicked motion of the surface dimers at room temperature. The flip-flop motion is mimicked by taking the average of the LDOS for the two dimer configurations (indicated by solid circles in Fig. 1). In addition we calculated the average of the buckled dimer positions and the constrained one, weighting each contribution by 1/3. This average roughly mimicks a sinusoidal oscillation of dimer buckling. The results of the simulations are given by the dashed and the dotted lines of Fig. 1, respectively. As the corrugation difference in the three last cases is less than 5 pm, these cases should not be distinguishable in STM measurements. In the rest of the paper we shall therefore simulate STM scans on clean silicon surfaces with the symmetric dimer surface.

IV. C_6H_6 ON Si(100): BOND LENGTHS AND ADSORPTION ENERGY

In order to estimate the structural changes due to bonding we computed the relaxed geometry of a single benzene molecule using the GGA exchange correlation.²³ The electron states are pure molecular states without dispersion. Benzene

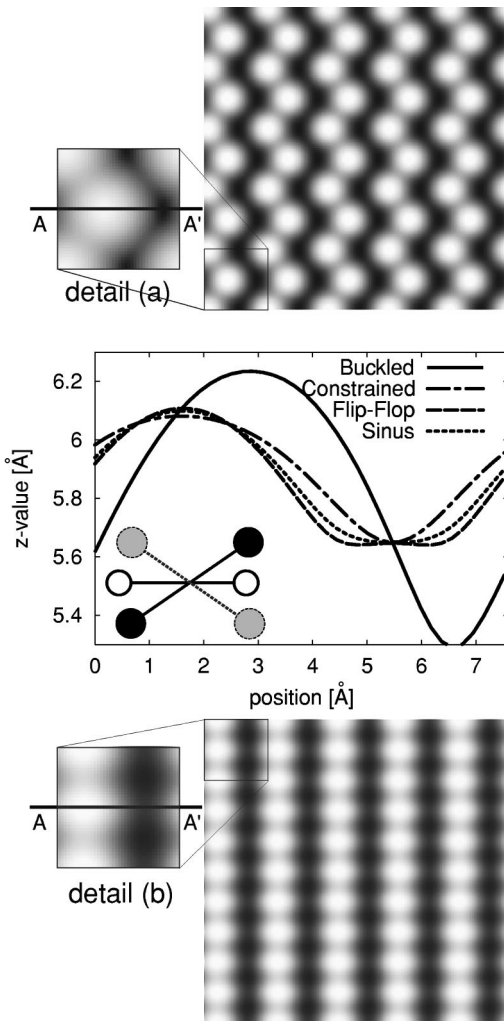


FIG. 1. Simulated line scan of clean surface along A , A' (see details): The position of the Si atoms is indicated by solid [buckled surface, detail (a)] and empty [constrained surface, detail (b)] circles. The plot gives the LDOS contour 10^{-8} states/eV of the surface electronic structure for four different cases: buckled surface (solid line), constrained surface (dash-dot line), flip-flop oscillations of the dimer (dashed line), and sinusoidal oscillations (dotted line). The three last cases are undistinguishable in STM images.

is a hexagonal, planar molecule with carbon bond lengths of 1.39 \AA , and the carbon-hydrogen bond is 1.09 \AA long.

In general, there are five geometries to be considered for adsorbed benzene. There are two single-dimer configurations. The (1,4) configuration symmetrically above a dimer [see Fig. 2, frame (a)]; and the (1,2) configuration, with adjacent carbon-silicon bonds on one side. In addition, there are three double-dimer configurations. The tight bridge configuration [Fig. 2, frame (b)], where the remaining double carbon bond is parallel to the silicon dimers; the twisted bridge, where the bond is perpendicular;⁶ and the symmetric bridge, where the carbon-silicon bonds are symmetric on either side of the molecule. We have performed simulations with VASP for all adsorption sites. The results are comparable to previous simulations using a cluster-based DFT method,⁶ although they differ somewhat in detail. For single-dimer

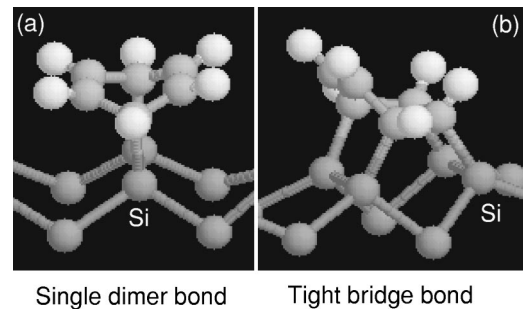


FIG. 2. Adsorption of benzene on Si(100). Adsorption on a single dimer distorts the planar geometry of the molecule. The highest protrusions in this case are at the positions of the double-bonded carbon atoms, symmetric to the silicon dimer. The tight-bridge configuration has its highest protrusion at the remaining double bond above one dimer.

adsorption the (1,2) configuration gives very low adsorption energies, indicating that this configuration is rather unstable. For the two-dimer adsorption the symmetric bridge is the least stable candidate. Calculations in this case did not arrive at a stable geometry at all. These two configurations are therefore excluded for theoretical reasons. The twisted bridge is in general only found in conjunction with a type-C defect:^{6,31} as we consider only adsorptions on a clean surface in the present paper, this case is also excluded. The remaining configurations, which can be unambiguously identified in STM measurements and confirmed by model simulations, are the single dimer (1,4) and the two dimer tight bridge configuration. Figure 3 shows an STM image at -1.5 V sample bias voltage at a constant current of 50 pA . Apart from the (1,4) and the tight bridge configuration (labels A and B) the image also shows the twisted bridge (label C), which is related to a surface defect.

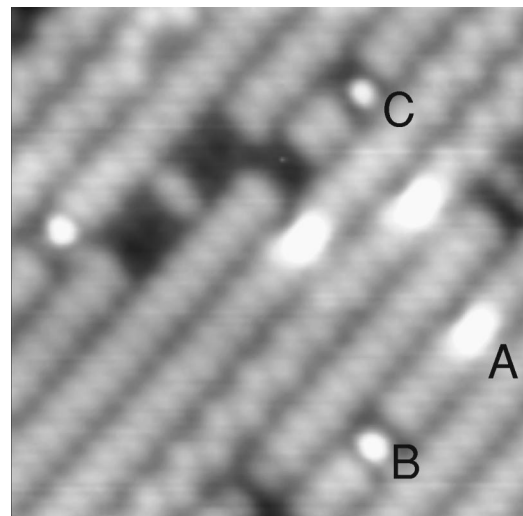


FIG. 3. STM scan of an Si(100) surface at room temperature ($U = -1.5 \text{ V}$, $I = 50 \text{ pA}$). The scan shows three different adsorption geometries for the benzene molecule. (A) Single-dimer (1,4) configuration. (B) Two-dimer tight-bridge configuration. (C) Two-dimer twisted bridge. Note that the apparent height is a maximum for the single-dimer configuration.

TABLE I. Bond length and adsorption energies of benzene on Si(100). The bond lengths and energies are nearly equivalent to the previously obtained values (B3LYP/6-31G*) (Ref. 10).

	C—Si (Å)	C—C (Å)	C=C (Å)	Energy (eV)
(1,4) Single dimer				
Gaussian	1.89	1.47–1.49	1.35	1.04
VASP	1.98	1.50	1.34	1.12
Tight bridge				
Gaussian	1.87–1.89	1.47–1.53	1.35	1.12
VASP	1.98–2.01	1.50–1.57	1.35	1.47

Initially, adsorption of benzene was calculated only for a (2×1) unit cell. But in case of the tight bridge configuration we observed much longer carbon-silicon bonds and a very low adsorption energy. Essentially, this result is due to the constraints of the setup: as no free dimers exist in a given row, the constraints on the adsorption geometry are somewhat artificial. However, the simulation predicts a lowering of adsorption energies at higher benzene coverage. The calculated energy difference (half a monolayer to one monolayer) is about 0.3 eV (1.42 eV versus 1.18 eV).

Adsorption energies of benzene in single-dimer and two-dimer configurations were obtained by calculating the energy difference between the independent molecule and the clean silicon surface and the fully relaxed combined system. To facilitate relaxation to the desired position we started relaxation cycles usually by setting the molecule roughly at the expected position. Convergence was achieved once forces on single ions were less than a threshold of 0.01 eV/Å. The results of our simulations are plotted in Fig. 2.

The (1,4) single-dimer configuration is symmetric with respect to the silicon dimer. The planar geometry of the benzene molecule is distorted to a V-shaped structure, where the double-bonded carbon atoms are substantially higher than the atoms bound to the silicon dimer [Fig. 2, frame (a)]. The Si-C bond length is 1.98 Å, the bond length to adjacent carbon atoms is 1.50 Å, a characteristic value for the expected sp^3 nature of the chemical bond. We note also a lengthening of the silicon dimer bond to 2.39 Å, a consequence of the weakened dimer bond due to the formation of new silicon-carbon bonds. The remaining double bonds have a bond length of 1.35 Å, again a characteristic value for organic molecules. The adsorption energy is 1.12 eV. The numerical values of the present simulations and the values previously obtained¹⁰ are given in Table I.

The tight bridge possesses four carbon-silicon bonds. The remaining double bond is parallel to the silicon dimers and bent from the silicon surface [Fig. 2, frame (b)]. The Si-C bond length in this case is about 2.0 Å; between bonding carbon atoms we obtain a slightly higher value than typical for single bonds, i.e., about 1.57 Å. The remaining double bond is 1.35 Å long, again characteristic of the double bond. The strain on the silicon lattice in this case leads to a notable distortion of the surface geometry: dimer bonds are lengthened to about 2.35 Å, while the distance between adjacent

dimers is shortened to 3.36 Å. The adsorption energy for the tight bridge configuration is 1.42 eV, or about 0.3 eV higher than the energy in the (1,4) site. The result indicates that this configuration is in fact more stable. It is the ground binding state of benzene on the Si(100) surface. An activation barrier of about 1 eV for the conversion from the single dimer to the bridge state is indicated by measurements;^{7,32} also the result that the bridge state is more stable is confirmed by STM measurements.

To estimate the influence of the geometry in the single-dimer case we have also calculated the adsorption geometry and the energy of benzene adsorbed across two dimers and with two carbon-silicon bonds. In a sense, the setup is a rotated (1,4) configuration. It seems, initially, more favorable than the single-dimer bond, because the dimer spacing of 3.8 Å is comparable to the distance across the benzene molecule in its ground state. The results in this case are similar to the unrotated (1,4) configuration. The adsorption energy remains unchanged and is 1.12 eV.

The combined evidence of experimental and theoretical research allows the unambiguous conclusion that the (1,4) single-dimer configuration is the metastable chemisorbed state of benzene, while the binding state is the tight bridge across two dimers.

V. C₆H₆ ON Si(100): SIMULATED STM IMAGES

Some preliminary conclusions can be drawn from the geometry and bonding characteristics of the molecule alone. The highest protrusion of the (1,4) single-dimer adsorption should be symmetric to the position of the dimer, where the two carbon double bonds reach the highest point above the surface. The excess of electronic charge at the location alone indicates a high overlap of tip and sample wave functions and thus, within the perturbation approach, a high tunneling probability. The same considerations for the tight bridge suggest a significant protrusion on top of one dimer and an unsymmetric structure. And finally it can be inferred that both molecule images in STM are symmetric with respect to a plane perpendicular to the dimer bond.

We initially assumed a spherical symmetry of the tip wave functions, in this case the tunnel current is proportional to the local density of states (LDOS) at the position of the tip.³³ From calculations of the current with a realistic tungsten tip we could obtain the vertical distance range common to measurements of about 50 nA tunneling current: the range is about 6.0 Å as the core-core (core of surface atom to core of tip apex atom, four dimers, unbuckled) distance. Since we used a plane-wave code for the sample wave functions, the range is already at the obtainable limit, even if we increase the vacuum layer to more than 12 Å. We therefore chose a contour closer to the surface, with a LDOS value of 5×10^{-7} states/eV. Figure 4 shows the results of our simulations. In the figure we have corrected slight deviations of the line scan zero point on the order of 0.1 Å from one system to the other, they describe the error margin of our method. The 5×10^{-7} states/eV contour for the clean surface exhibits only a small corrugation amplitude along the given line scan (0.2 Å, across dimer rows). The median distance from

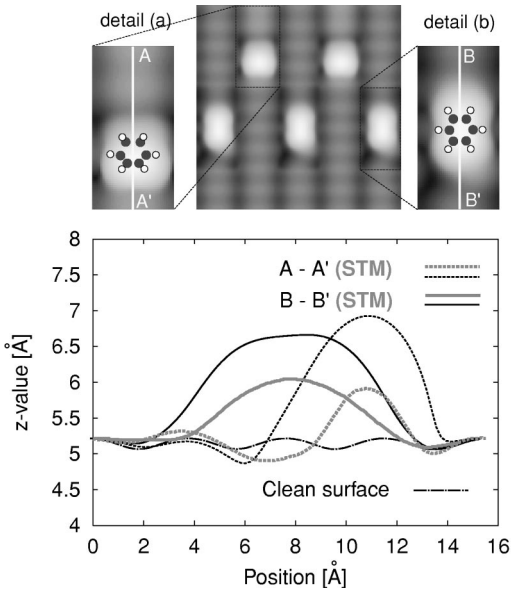


FIG. 4. STM images and line scans due to a LDOS contour of 5×10^{-7} states/eV. The simulation along $A-A'$ shows the highest corrugation (1.6 Å), it is due to the tight-bridge configuration. The scan on a (1,4) configuration, along $B-B'$ is lower, in the simulation, by about 0.2 Å. Experimental line scans (grey curves) are taken from a 50 pA constant current image.

the surface is about 5.2 Å. A benzene molecule, adsorbed either in the (1,4) position or in a tight-bridge configuration changes the shape of the contour drastically. In the first case the largest protrusion from the surface is about 6.7 Å, an increase of about 1.4 Å, measured from the highest protrusion of clean dimers. The molecule appears symmetric to a single dimer. The protrusion of the tight bridge configuration is 0.2 Å higher, and it is unsymmetric across two silicon dimers. The two cases should thus clearly be distinguishable in STM scans. The gray curves show measured line scans for a constant current contour of 50 pA. In both cases the measured images yield lower corrugation values than the LDOS contours suggest. One reason for the deviation is certainly the higher separation between sample and tip in the measurement. For exponentially decaying wave functions in the vacuum region an increase of the distance by 1 Å diminishes surface corrugation by a factor of about 2. The agreement is therefore rather good. This is at variance, with, e.g., simulations using the Tersoff-Hamann model at metal surfaces, where measured corrugations are usually higher.¹⁶ The deviation of the apparent height difference between the tight-bridge (higher in simulations, lower in measurements) and the single-dimer (1,4) configuration (lower in simulations, higher in measurements) could be due to the S-shaped tip orbital in the Tersoff-Hamann model. The apparent height difference between the tight-bridge and the (1,4) configuration vanishes, e.g., with a rhodium-terminated tip. Simulations with this tip will be shown in the next section. We note in passing that the simulated images are well in keeping with the simulations based on previous electronic structure calculations.⁶

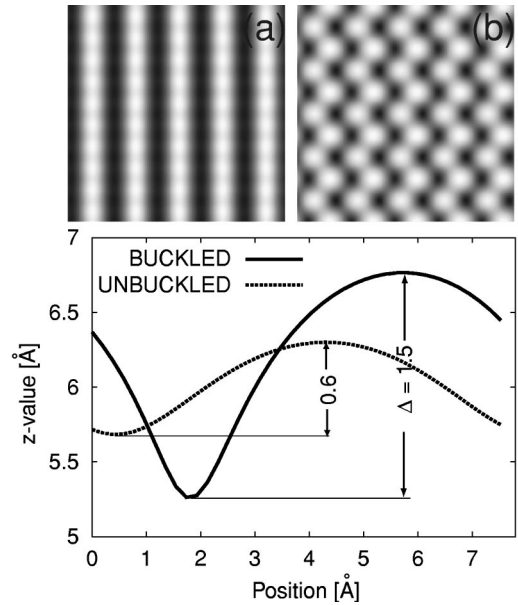


FIG. 5. STM images and line scans of a clean silicon surface scanned with a tungsten-terminated tip. The plots show a 40 pA current contour. The corrugation of the buckled surface is about 1.5 Å, of the symmetric or dynamically buckled surface about 0.6 Å. The STM image of the surface for both cases is shown in the top images [symmetric, detail (a), buckled, detail (b)].

VI. THE TIP STRUCTURE IN STM MEASUREMENTS

Generally, the chemical nature and geometry of the tip remains unknown in STM measurements. In order to resolve this problem one can perform controlled scans, where the sample and tip structure are known. Given the current precision and sophisticated combinations of different techniques, this procedure is not unrealistic. However, in the experiments described here the information about the tip cannot easily be provided. Therefore, we are limited to comparisons of experimentally obtained images or line scans and simulations. This entails, naturally, an educated guess about the tip. Notwithstanding adsorbates, we expect the tip to be terminated either by a tungsten atom or by an atom of the sample surface. The simulations with realistic tips have therefore been performed with a Si-terminated and a W-terminated structure. For the clean silicon surface we find good agreement for a tungsten-terminated tip. The simulated constant current contours at 40 pA and the line scans are shown in Fig. 5. The corrugation of unbuckled dimers is very high and about 1.5 Å. For the symmetric dimer we get a corrugation of 0.6 Å. The latter value is in keeping with experimental findings. The high value for the buckled dimer is suggested also by charge transfer from the lower atom of the dimer to the higher one. The overlap between tip and sample wave functions is therefore increased at the position of the high atom and decreased at the other one.

For benzene in a single-dimer (1,4) or tight-bridge adsorption, no agreement between measurements (see Fig. 6 for the line scans) and simulation can be obtained either with a tungsten- or with a silicon-terminated tip. In both cases we have a high contribution of d_{xz} and d_{yz} wave functions,

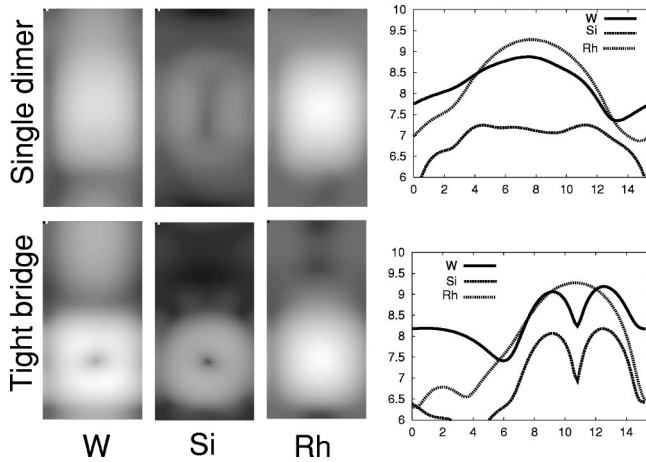


FIG. 6. Simulated images and line scans of benzene on Si(100) for three different tip structures. Tips terminated either by a tungsten or a silicon atom give results, which deviate from experimental values (see the line scans). The rhodium-terminated tip, which we show for comparison, gives better agreement, although also in this case the experimental observation of greater apparent height for the single-dimer bond is not reproduced.

which accounts for a shift of the current maximum compared to the LDOS maximum evaluated in the previous section. The results of our simulations are given in Fig. 6. It can be seen that both tips yield a minor minimum in the middle of the adsorbed benzene molecule for a tight bridge. On the single dimer the effect arises only for the silicon-terminated tip. This tip also yields rather low corrugation values. Since it is improbable that the tip changes from one adsorption site to the other, we conclude that neither of these tips is suitable to reproduce the measurements.

Analyzing the deviation it seems that the electronic structure, in particular the high contribution of d_{xz} and d_{yz} wave functions, is responsible. The LDOS already gives a rather good image of the real scans, suggesting that the actual tip in the scans was “sharper” than either the tungsten- or the silicon-terminated tip. In terms of wave functions, it has a higher contribution of s and $d_{z^2-r^2/3}$ wave functions. The best correspondence with this requirement was found, within the d metals, for a rhodium-terminated tip.³⁴ We show the results of simulations with this tip for comparison. The corrugation is substantially higher, the artificial minimum in the center of the molecule has vanished, and the apparent height of the single-dimer and the tight-bridge configurations are roughly equal. It seems thus that this tip is indeed better suited to reproduce experimental findings. Following this line of research we could pin down the problem to the structure of the tip. The tip models, tungsten films with a single apex atom were developed for simulating STM scans on metal surfaces. The corrugation on these surfaces is typically in the range of 10–20 pm.¹⁶ The corrugation of benzene on Si(100) is higher than 1 Å, a value that is already in the range of the interlayer distance of a tungsten film (1.6 Å). But in this case the overlap between tip and sample wave functions in an off-center position includes wave functions of the second layer. Since these contributions are unrealisti-

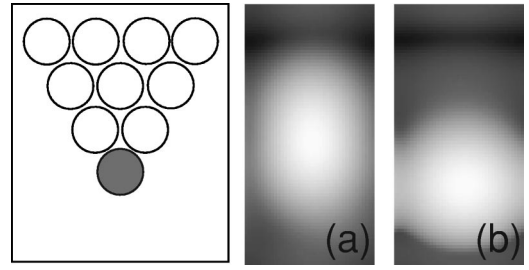


FIG. 7. Simulated images of benzene on Si(100) for a pyramid tip. The tip structure is a four-layer tungsten pyramid (left). The simulated images (current value of 50 pA) are the single-dimer species (a) and the tight-bridge (b) configuration. Simulations are in accordance with measurements, although, also in this case, the greater apparent height of the single dimer is not reproduced.

cally high for a film geometry of the tip, we modified the geometry to a pyramid-shaped structure (see Fig. 7). As demonstrated, the simulation of the scan in this case is in accordance with experiments. The only remaining discrepancy is a higher contour for the tight-bridge than for the single-dimer geometry. This deviation may be due to the overlap of tip wave functions with moleculelike wave functions of the benzene molecule. If these molecular states are highly localized, then their contribution to the tunnel current could be significantly lower than the mere overlap suggests.³⁵ We shall return to this point in future presentations.

VII. CONCLUSION

We have calculated adsorption geometries and bonding energies of benzene on Si(100). The metastable single-dimer and the stable tight-bridge configurations are confirmed as the predominant features in STM images. Calculated adsorption energies are well in keeping with experimental desorption data. The simulation of STM images on the basis of the electronic surface structure shows essentially the same features as the measurements; the numerical values, furthermore, obtained in these simulations are comparable with measured line scans. Simulations of STM scans with tungsten films and a single apex atom were in disagreement with experiments. We found that the disagreement is due to the geometry of the tip. A pyramid-shaped tip of four tungsten layers in (100) orientation was suitable to reproduce the experimental results. The result gives additional weight to the claim that the tunneling process is determined primarily by a single apex atom of the tip.

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