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Manipulation of benzene on Cu(110) by dynamic force microscopy: An *ab initio* study

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Based on *ab initio* calculations, we simulated how a single benzene molecule adsorbed on a Cu(110) surface can be mechanically manipulated by dynamic force microscopy using a clean silicon tip. Such a tip pushes the benzene molecule from one adsorption site to another and can therefore be used for lateral manipulation processes. On the other hand, a copper-terminated tip binds to the benzene molecule lifting it from the Cu surface.

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It is widely expected that the limit of miniaturization of electronic devices based on semiconductors such as silicon might be reached in the next few years.[1] As a consequence, the mainstream of current research is focused on the development of *nanometer-scale electronics* (nanoelectronics) based on single organic molecules (see, e.g., Refs. 2–4). In order to develop such devices, the imaging and manipulation of specific organic molecules are of fundamental importance. For conducting surfaces, the *scanning tunneling microscope*[5] (STM) is the tool of choice for this task because it enables simultaneous imaging and manipulation with atomic-scale resolution and precision.[6] This technique, however, is limited to conducting surfaces because it is based on the measurement of the tunneling current between an atomically sharp tip and the sample surface. Sometimes, it is possible to overcome this limitation by evaporating a thin insulator on a conducting surface. Repp *et al.*,[7] for example, evaporated a bilayer film of NaCl on copper in order to examine the bond formation of a gold atom and pentacene on an insulator.

However, future electronic nanoscale devices will consist of conducting and insulating parts.[8] Consequently, molecules have to be imaged and manipulated on both types of surfaces. A way out of this dilemma might be the *dynamic force microscopy* (DFM)—also known as *noncontact atomic force microscopy* NC-AFM[9,10]—which is not limited to conducting surfaces. This technique uses a sharp tip mounted on a silicon cantilever. The measured quantity is the change of the resonance frequency of the cantilever caused by the tip-sample forces.[11–13] The obtained resolution is comparable to the STM, and it is also possible to manipulate single atoms and molecules. To illustrate how molecules can be engineered at the nanometer scale, Loppacher *et al.*[14] measured the switching energy for the rotation of a porphyrin-based molecular switch. Another example is the work of Oyabu *et al.*[15] and Sugimoto *et al.*[16] who succeeded in manipulating single atoms on a semiconducting surface. Theoretical studies examined the lateral manipulation of a Ag atom on Si(001),[17] the vertical exchange of atoms on GaAs(001),[18] the lateral manipulation of vacancies on MgO(001),[19,20] and the imaging of organic molecules on TiO_2.[21,22] A combined experimental and theoretical study introduced an approach for the chemical identification of single atoms by DFM on Si(111).[23]

However, the majority of current studies still use the STM as a tool for the manipulation and imaging of specific organic molecules. Therefore, it is the purpose of this work to examine the potential of the AFM for the active manipulation of single organic molecules by employing state-of-the-art first-principles calculations. Since we were not aware of an experimental study where specific molecules were manipulated on purpose on a nonconducting surface, we had to choose a system which could potentially serve as a reference to compare STM and DFM experiments. Two conditions had to be considered in order to pick the right system: (i) isolated molecules have to adsorb on the substrate, and (ii) the bonding to the substrate has to be soft in order to allow a lateral manipulation of the molecule by the tip. These requirements are met by benzene (C_6H_6) adsorbed on a Cu(110) surface. It is well known from experimental STM studies[24,25] that single benzene molecules lay flat with very low coverage on a Cu(110) substrate. Furthermore, they can be easily moved along the $[\bar{1}10]$ direction.

The next issue to be considered is the chemical and structural nature of the tip used for the manipulation of the molecule. A standard material for STM tips are W or PtIr wires, while tips for DFM experiments are usually made of silicon.[12] Clean silicon tips can be prepared in vacuum by sputtering or annealing the tip (see, e.g., Refs. 26 and 27). Nonetheless, during the approach toward the sample surface, the tip might crash into the sample and some material might be picked up from the surface.[28] As a consequence, the exact geometrical and chemical nature is unknown in nearly all cases. We address this issue by the consideration of two chemically different tips: a clean silicon tip (Si_4H_3) with [111] orientation[29] and a copper-terminated tip, where the foremost tip atom was exchanged.

The electronic structure calculations are performed using *density functional theory* (DFT) within the generalized gradient approximation,[30] as implemented in the VASP code.[31–33] The electron-ion interaction is described by the *projector-augmented wave* scheme[34] with the electronic wave functions being expanded by plane waves up to a kinetic energy of 700 eV. Note that the current state of the art of the exchange correlation energy functionals used in DFT does not correctly describe the long-range van der Waals interactions. However, in NC-AFM simulations, the relevant forces are short-ranged, atomic-site specific, and correctly described by DFT. The complete system is modeled within the supercell approach by periodically repeated slabs, where each super-

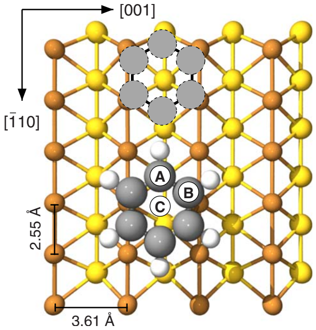

FIG. 1. (Color online) Ball and stick model of the Cu(110) surface and the benzene molecule. For better visibility, the second layer atoms of the copper surface are displayed in a lighter color (gray) compared to the first layer atoms. The so-called "long-bridge" site between two rows of the first layer Cu atoms has the lowest adsorption energy. The hexagonal structure in the upper part of the image indicates the so-called "hollow-site" position, which has a slightly higher adsorption energy. In the AFM simulations, we approached Si- and Cu-terminated tips at three different sites on the benzene molecule marked by A (on top of a carbon atom), B (carbon atom in "ortho" position to A), and C (center of the carbon ring). With a clean silicon tip, the molecule can easily be pushed along the [$\bar{1}$10] direction.

cell contains five atomic layers of copper plus the adsorbed benzene molecule with the tip on top. The vacuum region between the topmost atom of the tip and the next slab was larger than 15 Å. The calculations are performed with the theoretical Cu lattice constant of 3.63 Å using a $p(4\times 6)$ surface periodicity. The uppermost two copper layers, the benzene molecule, and the first atom of the tip are allowed to relax until atomic forces were lower than 0.001 eV/Å. In order to compensate for the dipole of the asymmetric slabs (since the benzene molecule and the tip are placed on one side of the slab), a dipole sheet is introduced in the middle of the vacuum slab.[35]

However, before including the tip into the system, we calculated the energetically favored positions of benzene on the Cu(110) surface. In agreement with experiments[24,25] and theoretical calculations,[36] we found that benzene is chemically adsorbed between two rows of atoms. The so-called "long-bridge" position where the benzene ring is on top of the two Cu atoms (see Fig. 1) has the lowest adsorption energy (−0.401 eV). However, the "hollow-site" position between four Cu atoms has an only slightly higher adsorption energy (−0.353 eV).

In STM experiments, the tip is laterally scanned over the sample surface. This is different in DFM experiments, where the tip vertically oscillates near the sample surface. As was done in previous studies,[18–20,23,28,29] we model this movement by a continuous approach and retraction cycle of the tip on top of the molecule. We considered three different sites and labeled them A, B, and C (see Fig. 1). Nonetheless, the overall outcome is independent of the specific molecular site used to approach and retract the tip. Consequently, we restrict the following discussion on short-range tip-sample forces calculated at the B site of the molecule.

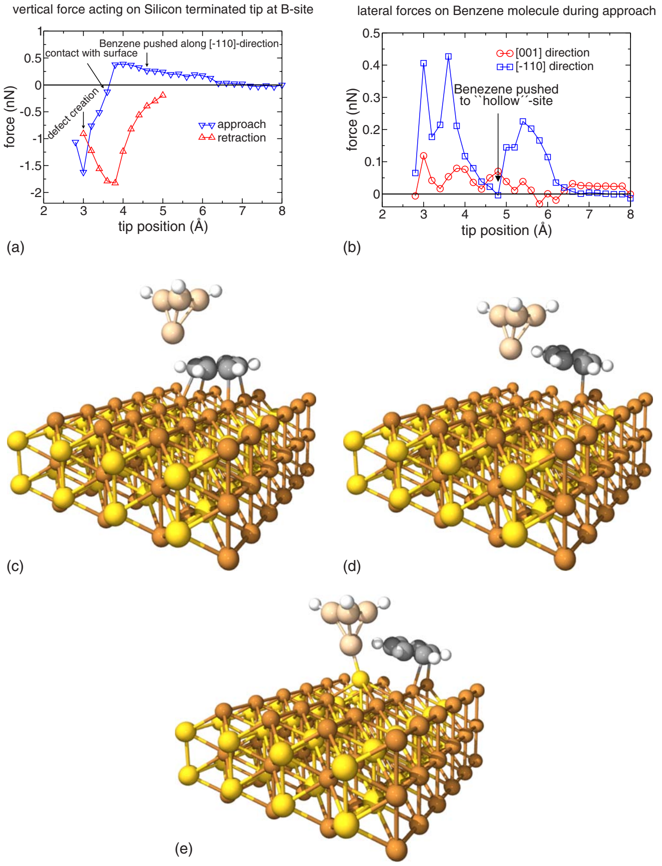

FIG. 2. (Color online) (a) Vertical force on the tip during approach and retraction for the clean silicon tip at the B site (see Fig. 1). The arrows mark the selected events shown in the ball and stick models. (b) Lateral forces acting on the benzene molecule along the [$\bar{1}$10] and [001] directions during the approach of the clean silicon tip. The arrow marks the tip position directly after the jump of the benzene molecule from the long-bridge to the hollow site. Here, the lateral force is initially zero. (c) During the approach, the benzene molecule is pushed along the [$\bar{1}$10] direction. (d) As the benzene molecule is moved away, the tip comes in direct contact with the Cu surface. (e) Finally, as the tip is pushed into the surface, an atomic defect is generated in the Cu surface.

Figure 2(a) displays the vertical tip-sample force during the approach and retraction of the *clean silicon tip* on the B site of the benzene molecule. The corresponding lateral forces acting on the benzene molecule along the [$\bar{1}$10] and [001] directions are shown in Fig. 2(b). The arrows mark some distinguished positions corresponding to the events shown in Figs. 2(c)–2(e). As the tip approaches the sample, the benzene molecule is closest to the apex of the tip. Therefore, the tip-sample force originates mostly from the interaction between the tip and the benzene molecule.

The wave function analysis of the frontier molecular orbitals shows that no bonding states between the tip and the molecule are formed; hence, the overall tip-sample forces are repulsive for this part of the force curve. Since benzene adsorbs on Si(100) (Refs. 37 and 38) and Si(111)7×7,[39] this feature of the silicon tip might be surprising at first sight. However, the different behaviors can be easily explained in terms of frontier orbital interaction theory of organic chemistry.[40] This implies that the highest occupied molecular orbital of the clean Si tip [$p_y(\sigma)$-like character] interacts with the lowest unoccupied molecular orbital of the adsorbed benzene molecule [$p_z(\pi)$-like character] and leads to a repulsive interaction.[41]

As a consequence of this repulsion, the benzene molecule is moved along the $[\bar{1}10]$ direction by the clean silicon tip. The lateral force plot shown in Fig. 2(b) reveals that the force needed to push the molecule from the long-bridge to hollow site is only 0.226 nN high. After the molecule is pushed away, the tip directly interacts with the Cu(110) surface atoms and the tip-sample force becomes attractive [see Fig. 2(c)]. As the tip is moved closer to the surface, the tip-sample force reaches a minimum. With the next step toward the surface, the foremost tip atom bonds to a first layer Cu atom. As the tip is retracted from the surface, this Cu atom is pulled out of the surface and a point defect is produced [see Fig. 2(d)]. The complete approach and retraction process is also available as an animation.[42]

It is important to note that due to the repulsive forces between the clean silicon tip and the benzene molecule, the molecule is also pushed along the $[\bar{1}10]$ direction for an approach and retraction on the *A* or *C* site (not shown). This peculiar behavior of the tip-sample system can therefore be associated with a controlled lateral manipulation of the benzene molecule. If the tip is approached to an appropriate distance between 2 and 4 Å, the molecule can be pushed by purpose from one adsorption site to another. A closer approach has to be avoided in order to prevent the generation of point defects, as shown in Fig. 2(e).

As discussed in the introduction, we also considered a *copper-terminated* tip which might be intentionally or unintentionally obtained during an approach toward the Cu(110) surface. In order to model such a tip in our simulations, we exchanged the foremost silicon atom with a copper atom. The complete approach and retraction curve was calculated in the same manner as that for the clean tip. Figure 3 summarizes the simulation results for an approach on the *B* site. An animation is available as additional material.[42]

The tip-sample force curve of the Cu-terminated tip [see Fig. 3(a)] looks quite different compared to the clean silicon tip. During the approach, the forces are quite small and oscillate around zero. Nonetheless, our simulations reveal a peculiar event during this approach. As shown in Fig. 3(b), the molecule detaches from the surface and bonds to the Cu atom at the tip apex. As has been observed for other metal-benzene organic compounds,[43] the binding energy between the Cu atom of the tip and the benzene molecule proved to be considerably strong and much larger than the attraction between benzene and the Cu(110) surface.

Moreover, we observed that this bond does not break during the complete approach and retraction path. As the tip goes further toward the surface, the benzene molecule is jammed between tip and surface, and the interaction forces become repulsive. During the retraction path, the tip-sample forces become attractive at a distance of 3 Å because benzene is now attracted by the surface and the tip. However, as mentioned before, the bonding between the Cu atom at the tip apex is stronger than the molecule surface attraction, and benzene is finally pulled away from the surface. The same attachment of benzene to the tip is also obtained for simulations on the *A* and *C* sites (not shown).

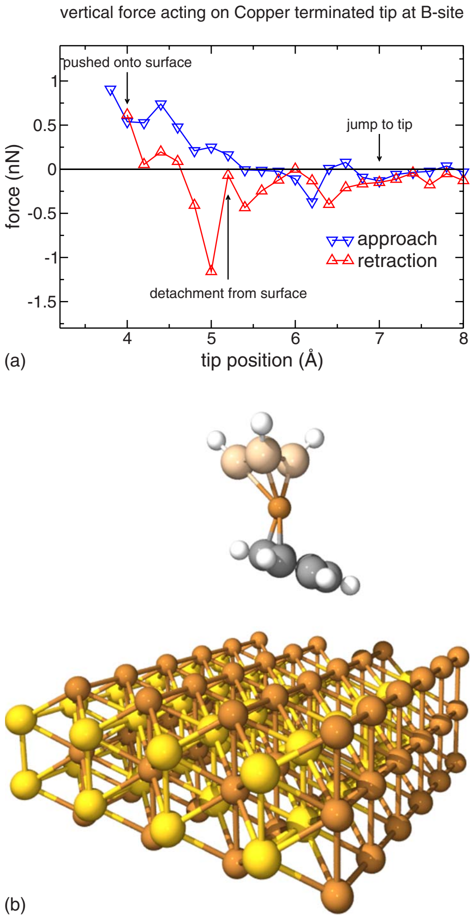

FIG. 3. (Color online) (a) Vertical force on the copper-terminated tip during approach and retraction at the *B* site. The arrows mark selected events. (b) Ball and stick model of the tip during the approach at a distance of 7.0 Å. Already at this comparable large distance, the benzene molecule jumps toward the tip and is covalently bonded. As the approach goes on, benzene is squeezed between the tip and the surface. Since the bonding between the benzene molecule and the Cu-terminated tip is more stable than the molecule and/or surface interaction, the molecule is moved away from the surface and the tip is terminated by benzene.

The energy required to detach the benzene from the tip is about 1.18 eV (compared to an isolated tip-benzene system). Therefore, it might be possible to remove the molecule from the Cu-terminated tip by an electric pulse in a similar fashion to STM experiments.[6]

In summary, we presented an *ab initio* study focused on the imaging and manipulation of single benzene molecules on a Cu(110) surface. Using two different types of tips, we observed a completely different interaction pattern between the foremost tip atom and the benzene molecule. For a clean silicon tip with a dangling bond the forces are repulsive, and the weakly bound benzene ring is pushed along the $[\bar{1}10]$ direction on the Cu(110) surface. On the contrary, the exchange of the tip apex atom by a copper atom results in a bonding between the aromatic molecule and the Cu atom. In this case, the bond between the Cu apex atom and the benzene molecule is stronger than that between the molecule and the substrate. Consequently, the benzene molecule is lifted from the surface and remains attached to the tip apex atom.

To conclude, our *ab initio* study clearly emphasizes that the chemical nature of the foremost tip atom plays a key role in the DFM imaging and manipulating process of organic molecules on surfaces. Therefore, our first-principles study is an important step in understanding how to tune the tip apex in order to perform the manipulation of organic molecules adsorbed on surfaces. Tip materials other than silicon and copper might be the focus of future studies in order to find an optimal tip material for the actual specific choice of organic molecules. Experiments based, for instance, on tuning fork sensors,[44] which enable us to choose nearly any material for the tip, can open a technologically reliable route to constructing nanodevices starting from isolated single organic molecules.

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[42] See EPAPS Document No. E-PRBMDO-77-100811 for an animation of the approach and retraction of the tip from and to the surface. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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