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Adsorption and electronic excitation of biphenyl on Si(100): A theoretical STM analysis

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Scanning tunneling microscopy calculations of a biphenyl molecule adsorbed on a silicon (100) surface allow disentangling the molecular adsorption's configuration as well as the electronic states whose excitation leads to the bistability response observed in recent experiments. The molecular configuration corresponds to one chemisorbed phenyl ring in a butterfly configuration. There is dissociation between the second ring and one hydrogen atom that passivates one Si dangling bond. The molecular motion is triggered by accumulation of charges in the resulting covalent Si-C bond formed between this latter ring and the surface.

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The control of the molecular motion on surfaces by mechanical or optical means has attracted a lot of work in recent years.[1] Understanding the mechanisms leading to this motion is then of great importance. In this context, scanning tunneling microscopy (STM) has become a powerful tool to explore structural and electronic properties of materials at the nanoscopic scale.[2–5] One striking feature is the possibility of manipulating individual atoms or molecules. The STM tip can be used to mechanically[6] or optically[3] control and manipulate these objects, but electronic excitation is emerging as a new promising way to control the molecular dynamics at the picometer scale inside a single molecule.[7,8] Based on this principle, outstanding experiments exhibiting bistable molecular configuration were presented in Ref. 7. The authors showed that biphenyl molecules adsorbed on Si(100) have two configurations that can be reversibly accessed by injecting electrons from the STM tip into the molecule.[7,9] The experimental evidence being clear, the nature of the electronic states excited with the tip and leading to the molecular switch is still unknown. Moreover, the geometry of the molecule adsorbed on the surface remains uncertain because STM does not give any direct image of the topography of the system. Simulations of STM imaging and spectroscopy are thus required to investigate the configuration of the molecule on adsorption as well as the electronic states involved in the excitation phenomenon.

In this Rapid Communication, we address these issues by means of (i) *ab initio* calculations to extract the possible configurations of the molecule when adsorbed and (ii) a tight-binding- (TB-) based STM modeling to compute images and spectra, providing compelling evidence about the true adsorbed structure. Furthermore, the investigation of electronic states at energies corresponding to the tip excitation will give new insights into the physical origin of the resonant states involved in the molecular motion.

The geometry of adsorbed biphenyl on the silicon surface has been calculated by *ab initio* density functional theory simulations.[10] The silicon surface is modeled by a slab made of four layers, each one containing 16 atoms. The lowest layer is passivated by hydrogen atoms [Figs. 1(a) and 1(b)]. Several local minima have been identified. The most energetically favorable geometry is represented in Fig. 1. As in the work of Mamatkulov *et al.*,[11] it corresponds to one phenyl ring adsorbed in the so-called butterfly configuration:[12] the ring, parallel to the surface, is attached to it through two Si-C chemical bonds. The second ring is twisted and linked to the surface through a single Si-C bond because of the loss of one hydrogen atom that passivates the dangling bond of the other silicon atom of the dimer. It is important to note that this adsorption's configuration is different from the one initially suggested in Ref. 7, as the adsorption induces the dissociation of the molecule by the breaking of a C-H bond. The activation energy for this phenomenon can easily be reached as the molecules are adsorbed at room temperature; the sample being cooled down afterward to perform the STM

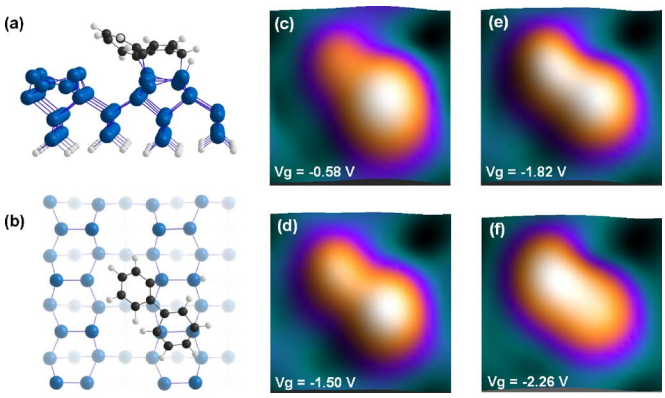

FIG. 1. (Color online) Front view (a) and top view (b) of the relaxed biphenyl on Si(100): one phenyl ring is adsorbed in a butterfly configuration whereas there is dissociation between the second ring and a hydrogen atom. This second ring is attached to the surface through a single Si-C chemical bond. The H atom is passivating one of the silicon's dangling bonds. Silicon, carbon, and hydrogen atoms are represented in blue (gray), black, and white, respectively. Calculated constant current STM images: I_t=0.12 nA and V_g=−0.58 V (c), V_g=−1.50 V (d), V_g=−1.82 V (e), V_g=−2.26 V (f). The color scale used to plot these images is black for a low height of the tip and white for a high one.

experiments.[7] To be consistent with the experimental labels, we will refer to these two rings as the mobile (Mo) and fixed (Fi) parts of the molecule, respectively.

In order to identify the true configuration of adsorption we used our TB technique to calculate STM images and scanning tunneling spectroscopy (STS) spectra of the adsorbed molecule. This model, described and compared to other existing methods in Refs. 13 and 14, has proved its efficiency on both surfaces and molecular systems, even for high applied biases.[15] The use of this semiempirical model is particularly suited, because of its rapidity and accuracy, to identify one configuration among many local minima. It also provides us with a more accurate STM image than just plotting the electronic density (i.e., using the Tersoff-Hamman method) calculated from the wave functions extracted from the previous *ab initio* calculations. The electronic structure of the system has been calculated using a self-consistent charge-density-functional-based TB method described in Ref. 16, for which the parametrization of the Hamiltonian has been validated on various molecular systems.[17] We have also checked that the relaxed structure obtained with that parametrized method is very similar to the one resulting from *ab initio* calculations. The tunneling current is calculated between the STM tip, which is assumed to have a pyramidal apex, and the sample. We used the Landauer formula in which the transmission coefficient $T(E)$ is expressed at each energy E in a Green's function formalism.[18] With this approach, we can include, in the calculations, effects of chemisorption upon electronic properties of the molecule. It is also possible to include tip effects although its geometry has only a weak influence on the calculations.[2] As in the work of Hofer *et al.*,[19] an alternative method to calculate STM images and STS spectra would be to use an out-of-equilibrium, or Keldysh, formalism. However, in our case, the tunneling current is rather small (0.12 nA). The transmission coefficient between the tip and the surface is then very low, so the charge transfer must be small. Thus, the self-consistency required in the Keldysh approach is not necessary here.

Constant current STM images have been calculated for several applied biases from −0.58 to −2.26 V and for a tunneling current of I_t=0.12 nA. As in the experimental setup, the bias V_g is applied to the sample, so that images obtained for negative polarizations reflect the contribution of the occupied states of the system. The calculated STM images are presented in Fig. 1. The simulations show an important dependence of the images with the applied bias. Just one strong bump is observed at low negative bias [V_g=−0.58 V, Fig. 1(c)]. It is mainly localized on the mobile phenyl ring of the molecule. When increasing the bias to −1.50 V [Fig. 1(d)] and −1.82 V [Fig. 1(e)], a second bump appears, more or less strongly, on the second ring. The image of Fig. 1(d) is very like the one observed experimentally[20] for V_g=−2.0 V [Fig. 1(c) in Ref. 7] as the fixed ring appears less bright than the mobile one. For a highly negative bias [V_g=−2.26 V, Fig. 1(f)], the main bump is shifting toward the fixed ring of the molecule but the transmission to the mobile part remains important. Moreover, as evidenced in the experimental measurements, a dark hole is observed right next to the fixed phenyl ring on the calculated images. This is a consequence of the passivation of the Si dangling bond by the dissociated

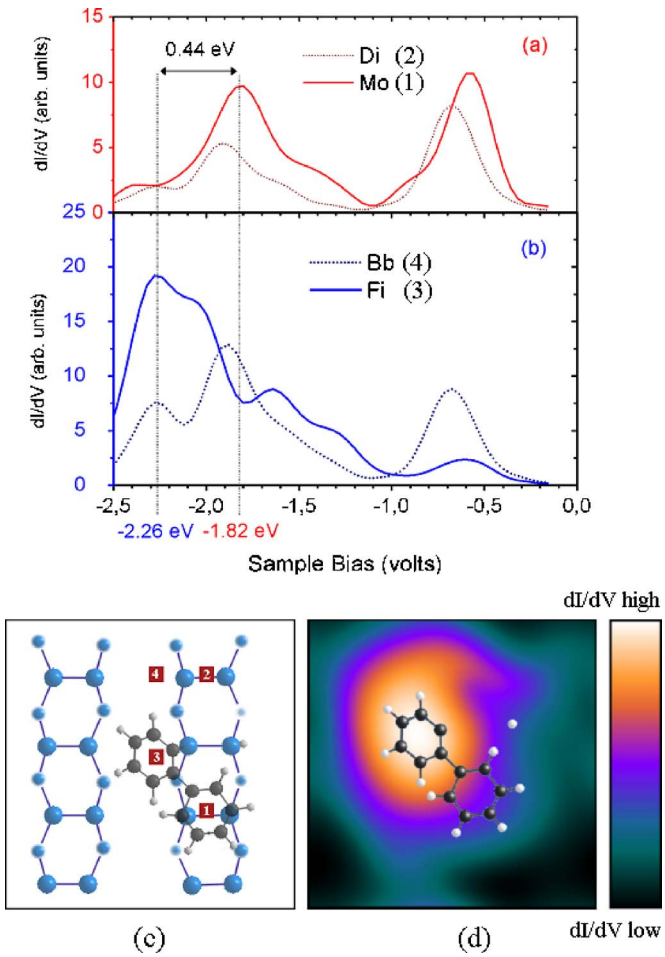

FIG. 2. (Color online) Calculated STS spectra for the Mo (plain line, 1) and Di (dotted line, 2) positions of the STM tip over the sample (a) and for the Fi (plain line, 3) and Bb (dotted line, 4) ones (b). Numbers (1 to 4) correspond to tip positions represented by squares on (c). (d) Topography of the dI/dV signal calculated at V_g=−2.26 V and I_t=0.12 nA with atomic molecular positions.

hydrogen atom. The very good agreement obtained with the experimental measurements thus demonstrates that the geometry of the system is different from the one originally assumed in Ref. 7. The structure of the system is more complex due to the dissociation and nonplanarity of the molecule. Moreover, the bias dependence of the calculated STM images strongly suggests the contribution of differently localized electronic states with respect to the polarization. To clarify that point, dI/dV curves have been calculated for four different positions of the STM tip over the sample [Fig. 2(c)]. The Fi and Mo labels refer to a tip located above the fixed and mobile phenyl rings, whereas the Bb and Di labels refer to a tip located between two silicon dimer rows or above a silicon dimer, respectively. Bb and Di positions correspond to the same relative positions over the silicon surface as Fi and Mo, respectively, but without the molecule.

As already demonstrated in our previous work,[21] the STS spectra calculated for the bare substrate [Bb and Di on Figs. 2(a) and 2(b)] do not depend on the position of the tip over the surface, for negative biases. The first peak in these two curves has been identified as a π surface state. On the other

hand, the comparison of the spectra obtained over the two phenyl rings of the molecule (Mo and Fi) highlights striking differences [Figs. 2(a) and 2(b)]. Due to very different shapes and relative intensities (in good agreement with the experimental observations; Fig. 4 of Ref. 7), the identification of the nature of the probed electronic states is less straightforward. The energy difference between the main peaks of each curve (0.44 eV) is very similar to the one measured experimentally (0.45 eV). As for the STM images, these differences suggest the contribution of electronic states differently localized inside the molecule (the authors of Ref. 7 labeled the main peak of each curve as π_1 and π_2, assuming that the two peaks result from the splitting of a π state of the molecule over the two rings).

The two spectra show a first peak at $V_g=-0.56$ V. It is very likely that this peak is associated with the silicon π surface state.[22] The nature of this electronic state is consistent with the STM image calculated for $V_g=-0.56$ V, as a single predominant bump is observed over the mobile ring. We are probably in a situation close to the one already found for conjugated oligomers on Si(100),[13] where the properties of the surface were enhanced by the presence of the molecule. The main differences between the Mo and Fi spectra arise for high negative biases. The peak obtained for the Fi position at $V_g=-2.26$ V is not observed when the tip is placed over the Mo phenyl ring. Moreover, at this energy the dI/dV curve over the Mo part exhibits a minimum of intensity; the main peak in this spectrum being obtained for $V_g=-1.82$ V. Thus, the two electronic states probed by STS measurements at different locations over the molecule correspond to very localized states on different parts of the molecule. One way to visualize this localization is to plot the dI/dV signal image for a bias corresponding to one of the STS peak. Experimentally, such an "image" can be recorded using a lock-in amplifier when acquiring the topographic image. We computed it by numerical discretization of the derivative of the tunneling current with respect to the applied bias, i.e., we first calculate the standard STM image. The z positions of the tip are then determined to get the proper current (0.12 nA). From these tip heights we calculated the dI/dV signal by varying the voltage around $V_g=-2.26$ V and by determining the corresponding current. The dI/dV signal can then be plotted as a function of the (x,y) position of the STM tip. The result of such an image is presented in Fig. 2(d). The maximum of the signal is located only on the Fi ring, which is consistent not only with the STS curve but also with the experimental observation (Fig. 4 in Ref. 7). This result definitely confirms the strong localization of the electronic contribution over the fixed part of the molecule, at this energy.

This spectroscopic study allowed us to reproduce, with very good agreement, the experimental observations. Two very different spectra have been obtained, reflecting differently localized electronic states, at the scale of the molecule itself. This definitely confirms the finding of the true adsorption's configuration of the biphenyl on the silicon surface. Furthermore, the two different main peaks observed in the STS spectra correspond to the energies at which the molecule can be electronically excited to induce the molecular switch. The simulation of the bistability path of the molecule would require a self-consitent calculation of the tunnel junction geometry with carrying current. The work of Emberly and Kirczenow[8] has shown that such STM-induced phenomenology can be understood, on simpler models, by means of full *ab initio* calculations. This is, however, beyond the scope of this paper. However, it is of fundamental importance to get a more detailed analysis of the nature of the excited states, in order to get first insights into the mechanisms responsible for the bistability phenomenon. The modulus of the wave functions of the system has been integrated over a small energy window of 0.2 eV around the two main peaks observed in the STS spectra. Hence, we have plotted, in Fig. 3, the electronic density for energies $E_1=-1.82$ eV and $E_2=-2.26$ eV corresponding to the STS peaks obtained over the Mo phenyl ring and the Fi one, respectively. We have integrated this density over a small energy window as it should be more consistent with experimental STM measurements. Not surprisingly, the density calculated for E_2 is strongly localized on the Fi part of the molecule [Figs. 3(c) and 3(d)] consistently with spectroscopic curves and imagery. We can also note that an important part of the density is located on the Si-C chemical bond between this ring and the silicon dimer. On the other hand, the density calculated for E_1 is almost exclusively localized on the same Si-C bond [Figs. 3(a) and 3(b)] and only a small part on the mobile ring. This is an important difference from the experimental analysis which assumed that this state would be mainly localized on the mobile ring. We proved here that the two peaks observed in the spectroscopic study are not only the result of a splitting of a π molecular state, the contribution of the Si-C bond being very important. This result also suggests that the excitation of the electronic states associated with this Si-C bond could be responsible for the experimentally observed molecular motion. Indeed, in Ref. 7, the biphenyl

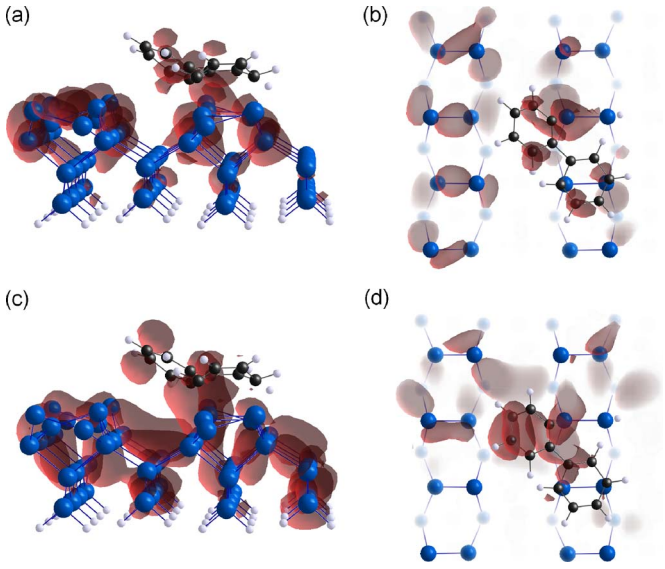

FIG. 3. (Color online) Front view (a),(c) and top view (b),(d) of the electronic density integrated over a 0.2 eV window around $E_1=-1.82$ eV (a),(b) and around $E_2=-2.26$ eV (c),(d).

molecule can be switched from one stable position to the other one when exciting with the STM tip, over either the Mo or the Fi part of the molecule. However, the efficiency of the molecular switching is more important when injecting electrons over the Fi ring. From these calculations, we showed that both excitations could activate the same mechanism. A greater switching rate is obtained when exciting the Fi ring because of the stronger localization of the corresponding state on this phenyl group.

In conclusion, we have shown, by *ab initio* calculations and semiempirical STM simulations, that the adsorption configuration of biphenyl on Si(100) is different from the one originally proposed by Lastapis *et al.*[7] We confirmed the contribution of differently localized electronic states at the scale of the molecule itself. In contrast to the experimental hypothesis, we have shown that the excited electronic states leading to the molecular motion are localized not only on one or the other of the two phenyl rings, but also strongly along the Si-C bond between the fixed phenyl ring and the surface. This work opens the way to more sophisticated molecular dynamics calculations in order to get a glimpse at the path followed by the molecule during its bistability movement.

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