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Chemisorbed bistable molecule: Biphenyl on Si(100)-2×1

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We have shown that the room-temperature adsorption of the biphenyl molecule on the Si(100) surface gives rise in majority to a bistable molecular configuration. The switching of the bistable molecule is activated at room temperature by thermal activation. By using a combination of room-temperature and low-temperature (30 K) scanning tunneling microscope (STM) topography, room-temperature STM manipulation, and near edge x-ray absorption fine structure spectroscopy, the nature of the bistable molecule, its adsorption geometry, and its interaction with the surface could be identified.

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I. INTRODUCTION

Nanometer-scale molecular architectures, made of *individual* molecules adsorbed on a surface, are becoming of crucial interest in many fields of science and technology, in particular in molecular electronics.[1] The use of future complex molecular architectures as real nanomachines requires the design of basic functions. One of the most important functions to be designed is a bistable molecular device, which may serve for fabricating atomic-scale switches, clocks, memories, or logic circuits. Ideally, a bistable molecular configuration should, in a molecular architecture context, have two *equivalent* stable states which can be easily switched from one to the other. So far, no such bistable molecule could be found although several examples of reversible[2–9] or irreversible[10–12] movements of molecules on surfaces exist. Indeed, previous examples exhibited nonequivalent stable states[2–8,10] or more than two equivalent states.[9] In this paper, we propose that biphenyl molecules adsorbed on Si(100) offer a unique opportunity for experimenting with a bistable molecule.

The adsorption of biphenyl molecules on Si(100) is an interesting system to be studied since the molecules do not dissociate and show a range of adsorption configurations. When adsorbed at low temperature (30 K), the molecules are physisorbed. At room temperature, the molecules can be either weakly or strongly chemisorbed on the surface. Room-temperature scanning tunneling microscope (STM) topography and manipulation, low temperature (30 K) STM topography, and near edge x-ray absorption fine structure (NEXAFS) spectroscopy of the weakly chemisorbed configuration demonstrate that this configuration is a bistable molecule.

II. EXPERIMENTAL

The STM experiments were performed both at room temperature and low temperature (35 K) in an ultrahigh vacuum (UHV) chamber (base pressure 2×10^{-11} Torr) using a room-temperature scanning tunneling microscope and a variable temperature STM. With the variable temperature STM, the sample can be cooled down to 35 K using a helium liquid flow cryostat. For room-temperature experiments, the Si(100) samples were *p*-type B doped with a resistivity of 1 Ω cm. At low temperature, we used highly As-doped *n*-type Si(100) (bulk resistivity of 0.004 to 0.007 Ω cm). The silicon samples were first outgassed for at least 12 h at 700 °C before flashing to 1080 °C to remove the surface oxide layer. The duration of each flash was adjusted such that the pressure remained below 1×10^{-9} Torr.

The STM has been used in both the topographic and manipulation modes. In the manipulation mode, the STM tip is held at a fixed position above the surface over a selected molecular site. After positioning the tip, the feedback loop is switched off, a positive voltage V_s is applied to the surface during a certain time (50 ms). For each manipulation, the tip-surface distance is adjusted to obtain a given tunnel current as measured by an oscilloscope. Afterwards, the STM topograph of the same area is recorded to check the result.

III. RESULTS AND DISCUSSION

A. Room-temperature experiments

The STM image of the Si(100)-2×1 surface after the adsorption of 0.1 L of biphenyl at room temperature is shown in Fig. 1. Two adsorption configurations can be seen; nine sites which seem unstable as if each molecule is moving (they look striped in Fig. 1) and one site that appears stable as if the molecules are fixed (circled). These two configurations occur, respectively, 80 and 15 % of the time (a site that appears to be the result of a dissociation is sometimes seen at higher exposures). The other bright features in Fig. 1 are due to defects already present before exposure. For exposures of biphenyl between 0.02 and 0.1 L, the sticking coefficient was found to be in the range 0.07 to 0.2. Additional results are shown in Fig. 2. Figures 2(a) and 2(c) are two areas of the clean surface showing a few defect sites (dark sites). Figures 2(b) and 2(d) are the same areas after exposure to 0.1 L of biphenyl. Five striped sites are seen in Fig. 2(b) whereas two striped sites and three fixed (circled) sites are seen in Fig. 2(d). From this, it is clear that the biphenyl molecules adsorb on clean areas of the surface and the adsorption seems to be not affected by defects. STM images of Figs. 2(e) and 2(f) are identical to those of Figs. 2(c) and 2(d), respectively, except that the sample voltage has been changed from −2 to +2 V. The fixed sites have a higher electron density of unoccupied states than the striped sites [Fig. 2(f)] and the striped sites are striped in both polarities.

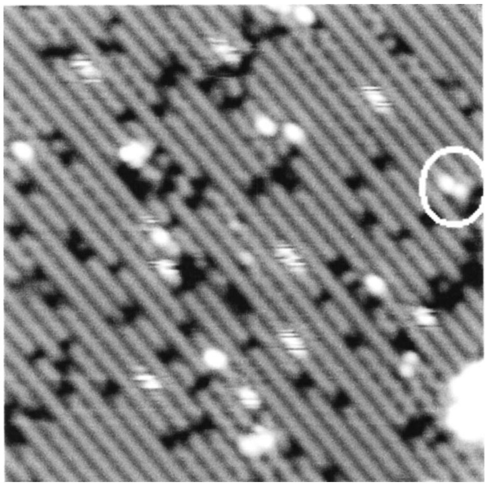

FIG. 1. Room-temperature filled state STM topograph (200 Å ×200 Å) showing the Si(100)-2×1 surface after exposure to 0.1 L of biphenyl. As a result of the adsorption there are nine sites that appear to be in motion and 1 fixed site (circled). The tunnel conditions were −1.5 V and 0.5 nA.

The unstable configuration or striped site is shown in detail in Fig. 3(a). It can be seen that the species is in motion as the tip passes over it. However, the STM tip did not appear to influence the motion of the molecules. Indeed, from an analysis of the length of the stripes visible in the STM images of several striped molecules [Fig. 3(a) shows one of them], it was possible to extract a frequency for the motion of the molecule. The extraction of a frequency is only valid if individual strips are shorter than the width of the molecule. This was true for more than 50% of the lines in each molecule studied. Several molecules were analyzed as a function of scan speed. When the scan speed was slow ($<30\ \mathrm{nm\,s^{-1}}$), most lines were made up of bright streaks (molecule present in the tunnel junction) separated by dark sections (molecule absent). The frequency extracted in this way was found to be about 100 Hz. The frequency was found to be independent of the tunnel current and sample voltage, i.e., of the tip-surface interaction. It follows that the motion must be thermally activated. Assuming a preexponential factor of $10^{13}\ \mathrm{s}^{-1}$ in the Arrhenius equation, the barrier for the motion can be estimated to be about 0.64 eV. It is important to note that the unstable configuration has never been observed to diffuse over the surface under normal scanning conditions.

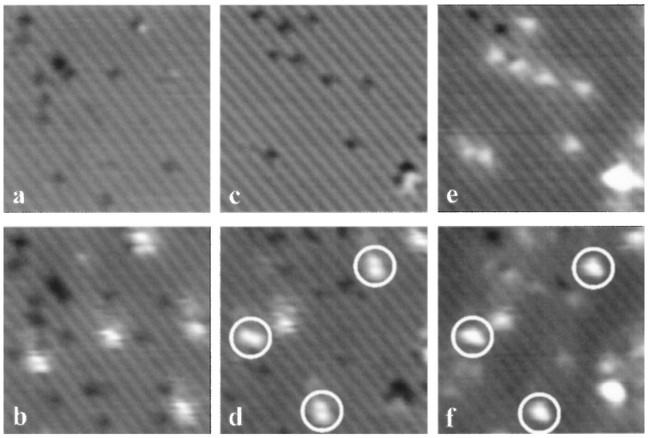

FIG. 2. Room-temperature STM topographs (130 Å×130 Å) of the Si(100)-2×1 surface recorded before [(a), (c), (e)] and after [(b), (d), (f)] exposure to 0.1 L of biphenyl. (a) and (b) are filled state images ($V_s = -2$ V, $I = 0.5$ nA) of a first region. (c) and (d) are filled state images ($V_s = -2$ V, $I = 0.5$ nA) of a second region and (e) and (f) are the corresponding empty state images ($V_s = +2$ V, $I = 0.5$ nA).

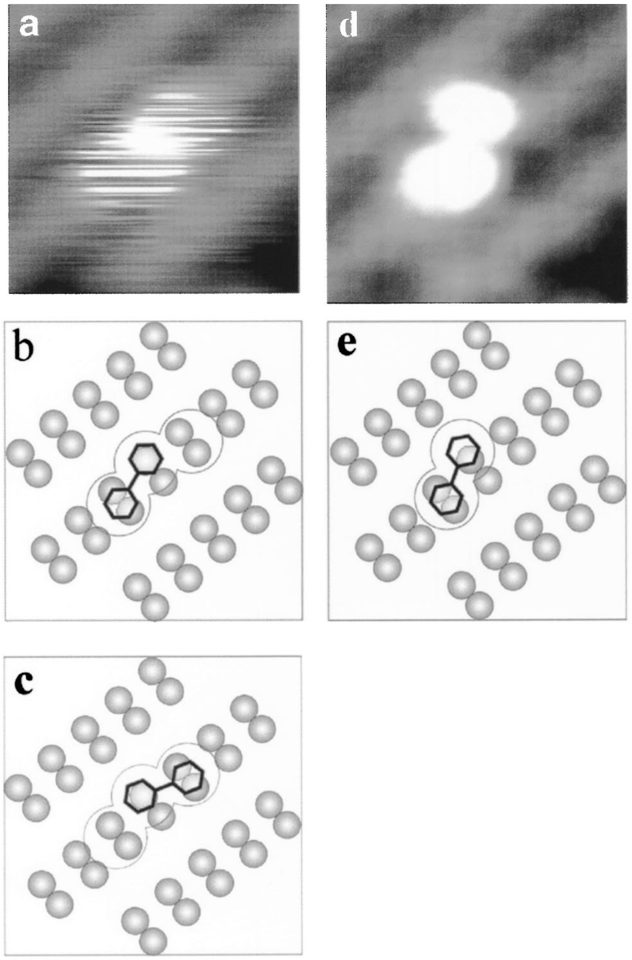

FIG. 3. A zoom of a room-temperature filled state image (25 Å×25 Å, −1.5 V and 0.5 nA) of a bistable site is shown in (a). Two possible binding configurations which fit within the envelope of the bistable site are shown in (b) and (c). The fixed site shown in (d) is the result of manipulating (+3.7 V pulse) the bistable site in (a). This fixed site appears identical to the fixed sites resulting from the direct adsorption of the biphenyl from the gas phase. A diagram of the possible adsorption configuration is shown in (e).

Interesting complementary information on the unstable configuration has been obtained by using the STM in the manipulation mode. Two different kinds of manipulations are illustrated in Figs. 3 and 4.

For a sample voltage of +3.7 V and a tunnel current of 10 nA, 21 out of 22 attempts transformed the unstable site [Fig. 3(a)] into a fixed state [Fig. 3(d)] and one displaced it across the surface by about 30 Å. The fixed site produced by manipulation is exactly the same as the one spontaneously pro-

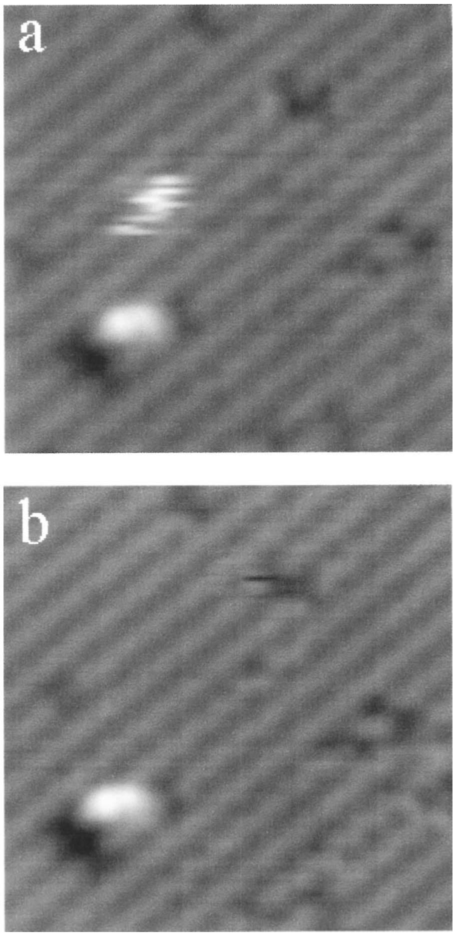

FIG. 4. Two room-temperature filled state STM topographs (each 100 Å × 100 Å, −1.5 V and 0.5 nA) showing in (a) a bistable site and a fixed site. Subsequently, a +6 V pulse was applied to the bistable site and the result is shown in (b)—the bistable site has been removed revealing the clean surface underneath.

duced by molecular adsorption. A detailed look at the fixed site [Fig. 3(d)], shows two bright protrusions, one centered on the dimer row on top of a dimer and the other in between the dimer rows [the position of the bright protrusions relative to the silicon dimers cannot be clearly seen in Fig. 3(d) because of their very different corrugations]. The angle between a line through the protrusions and the silicon dimer row is 30°. On only five occasions out of 57 was a molecule seen to adsorb with its major axis at 60° to the dimer row direction. The distance, between the centers of both protrusions, measured from a line profile is 0.45 nm. This would suggest that we are seeing the intact molecule chemisorbed on the surface since the expected distance between the centers of two phenyl groups in the free molecule is 0.43 nm. A proposed adsorption configuration is given in Fig. 3(e).

For a sample bias of +6 V and a tunnel current of 50 nA, eight out of ten attempts removed the unstable site from the surface (Fig. 4) and two transformed the unstable site into the fixed site. As seen in Fig. 4(b), the area of the surface where the unstable site was, is free of any defect.

These manipulation experiments indicate that the unstable site corresponds to a single biphenyl molecule adsorbed on the clean Si(100)-2×1. From the STM image of the unstable site [Fig. 3(a)], it seems that the molecule oscillates between two positions with a brighter fixed point in the center. Each position, as seen from the envelope of its striped image, corresponds to a molecule with an axis at about 20° to the silicon dimer row direction. The brighter fixed point is located on top of one of the silicon atoms of a dimer. A schematic diagram indicating the two positions of the bistable molecule are shown in Figs. 3(b) and 3(c). The envelope surrounding the phenyl rings is intended to represent the extension of the electron density visible in the STM images. The contours are based on the visual size of the molecule in its fixed site (FWHM of a line profile). The adsorption configurations of the unstable site shown in Figs. 3(b) and 3(c) have been derived from the examination of many unstable sites similar to the one in Fig. 3(a). Although it is difficult to ascertain these adsorption configurations only from the observation of the striped sites, we will see in the following that low-temperature experiments confirm these configurations nicely.

The STM enabled us to evidence the bistable molecule and to suggest its geometry on the surface. However, it says little about the nature of the bonding of the molecule, i.e., whether the molecule is physisorbed or chemisorbed on the surface. For that, we performed near-edge x-ray fine structure (NEXAFS) spectroscopy using the super-ACO synchrotron radiation source at Orsay. The experimental setup has been described previously.[13] The partial electron yield measured for 268 eV electrons [corresponding to the maximum intensity of the C(1s) Auger electron spectrum] was recorded as a function of the photon energy around the C(1s) threshold. Several NEXAFS experiments were carried out on the Si(100) surface as a function of biphenyl exposure and temperature as well as the incidence angle of the synchrotron radiation.[14] A series of NEXAFS spectra of the transitions between the C(1s) level and the antibonding orbitals are shown in Fig. 5. These could be compared to existing NEXAFS experiments on benzene adsorption on the same surface.[15] If we consider the multilayer exposure at 80 K, where one can expect the molecular orbitals to be similar to those of the molecule in the gas phase, we see three peaks at 285, 287.5, and 289 eV. In a core excitation experiment it is difficult to place correctly the unoccupied levels with respect to the Fermi level. It is expected to be at around 284 eV. This would place the first π state at 1 eV. The three peaks are exactly the same energies as in a multilayer of benzene[15] and are believed to correspond to an excitation of a C(1s) electron into the unoccupied (π^*_1,π^*_2), $\sigma^*_{\text{(C-H)}}$, and π^*_3 orbitals of the aromatic ring. This identity of the spectra of benzene and biphenyl has been previously observed in gas phase NEXAFS data[16] and has been explained by the localization of the unoccupied orbitals after C(1s) excitation. In the submonolayer regime, at 80 K, where the biphenyl molecules are expected to be physisorbed on the surface, the C(1s) spectra look almost identical except that the peaks are somewhat broader due to the interaction with the surface. Quite interestingly, at room temperature, the π^*_3 peak at 289 eV is no longer visible. It has been previously demonstrated in the case of benzene that the absence of the π^*_3 orbital in

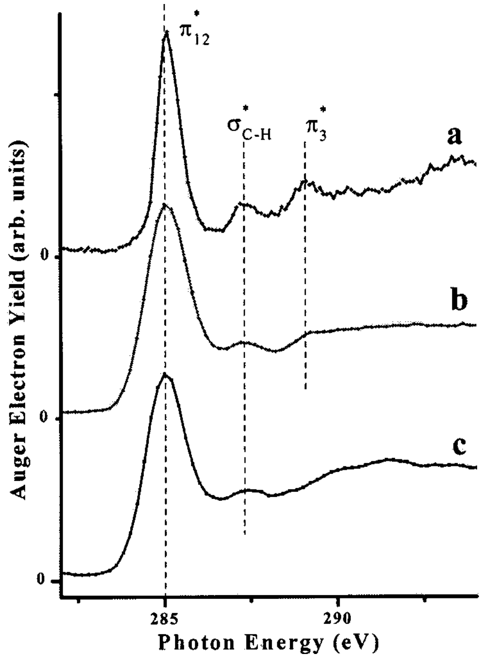

FIG. 5. A graph showing the NEXAFS spectra of biphenyl adsorbed on the Si(100)-2×1 surface. The Auger electron yield is given as a function of the photon energy around the C(1*s*) threshold for (a) a multilayer exposure (10 L), (b) a submonolayer exposure at 80 K (0.45 L), and (c) a submonolayer exposure at 300 K (0.5 L). The curves have been shifted vertically relative to each other for clarity.

the NEXAFS spectrum is indicative of a chemisorbed interaction with the surface.[15] This suggests that the biphenyl is physisorbed at low temperature and chemisorbed at room temperature. Thus, at room temperature, the STM images, where the bistable molecule is in the majority, show a ‘‘chemisorbed’’ molecule that moves. The movement of the bistable molecule suggests that the molecule is only weakly chemisorbed whereas the fixed molecule [Fig. 3(d)] is considered to be strongly chemisorbed. The corresponding configurations of these weakly and strongly chemisorbed molecules will be discussed in Sec. III C.

B. Low-temperature experiments

From the estimated energy barrier for the motion of the bistable molecule (0.64 eV), the movement of the molecule should be easily frozen at low temperature. To verify the adsorption configuration of the bistable molecule, we exposed the clean Si(100) surface to 0.1 L of biphenyl at room temperature. After exposure, the sample was cooled down to 35 K and the surface was imaged by using the variable temperature STM. Contrary to the observation at room temperature, no striped site was seen at low temperature where only fixed molecules were observed (Fig. 6). All the observed molecular sites show two bright protrusions. The distance between the centers of the protrusions is 0.44 nm and the angle between a line through the protrusions and the silicon dimer rows is about 20°. This angle is determined with a precision of ±5° and is definitely smaller than the 30° angle of the fixed sites seen at room temperature (Figs. 1 and 2). It is clear from this result that, at low temperature, the bistable molecules are all fixed in one of their two stable positions shown in Figs. 3(b) and 3(c).

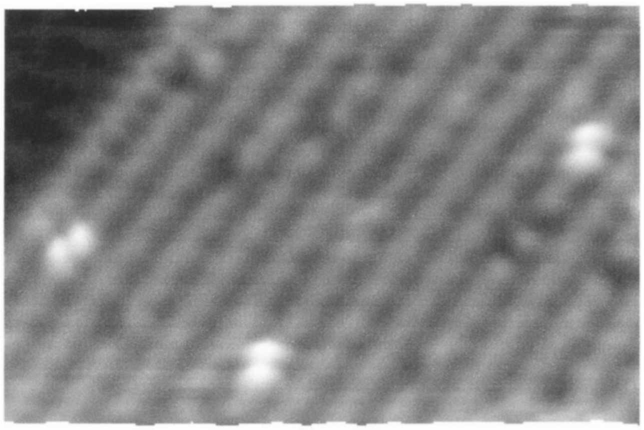

FIG. 6. Low-temperature (35 K) filled state ($V_s = -1.5$ V, $I = 0.5$ nA) STM topograph (150 Å×100 Å) of the Si(100)-2×1 surface exposed at room temperature to 0.1 L of biphenyl.

Complementary experiments were performed by cooling down first the silicon sample to 35 K and then exposing the surface to 0.1 L of biphenyl. Very different molecular sites were obtained under these conditions as seen in Fig. 7. They consist of a single bright protrusion centered on the silicon dimer rows. However, all the molecular sites show an associated secondary feature on the neighboring silicon dimer row. The secondary feature has a much lower intensity. It is not due to any tip effect since its position relative to the main

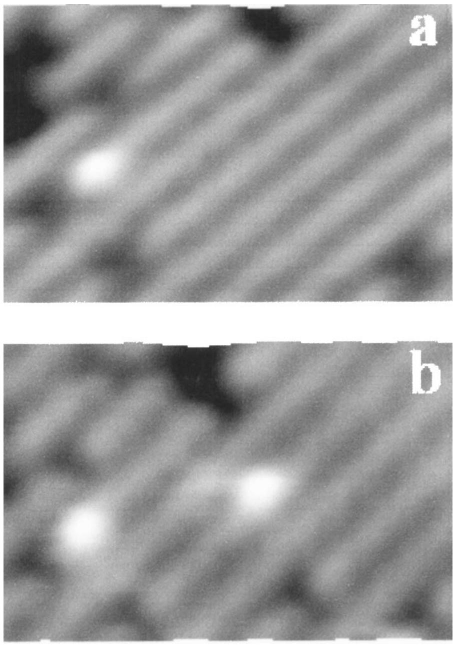

FIG. 7. Low-temperature (35 K) filled state ($V_s = -1.5$ V, $I = 0.5$ nA) STM topographs (90 Å×60 Å) of the Si(100)-2×1 surface before (a) and after (b) exposure to 0.1 L of biphenyl at low temperature.

bright protrusion varies from one molecule to the other. The exact molecular configuration is more difficult to elucidate than for the bistable molecules and the fixed molecules at room temperature. Here, one can anticipate that the molecules are physisorbed and that the main bright protrusion corresponds to one of the two phenyl rings weakly interacting with the silicon dimer row. The molecule would then stand up on the surface with the second phenyl ring oriented towards the neighboring dimer row giving rise to the weak secondary feature. This needs to be verified by further calculations and experiments. However, it is already clear that the biphenyl molecules adsorb very differently at low temperature.

C. Discussion

From these observations, a model for the adsorption of the weakly chemisorbed bistable and the strongly chemisorbed stable configurations can be developed. We already discussed in Sec. III A the bonding configurations for the bistable and stable sites [Figs. 3(b), 3(c), and 3(e), respectively] as derived from the room temperature STM experiments. The low-temperature experiments (Fig. 6) confirm that the metastable sites of the bistable molecules are indeed those shown in Figs. 3(b) and 3(c). As to whether the motion is a translation along the row or a rotation about a fixed point, a rotation [as shown in Figs. 3(b) and 3(c)] seems far more likely since nothing would prevent a translation continuing along the row for some distance, yet the striped site occupies only three dimers.

In the bistable state [Figs. 3(b) and 3(c)], each phenyl ring of the biphenyl molecule can interact with a silicon dimer or a silicon atom. However, no σ-σ valence bond between C and Si atoms is expected to occur, or at least significantly weakened bonding if it does. Indeed, such σ-σ valence bond between C and Si atoms would strongly bond the molecule with the surface and would prevent the bistable molecule to oscillate from one position to the other. Since we know from the NEXAFS spectra that a chemisorbed interaction nevertheless exists between the bistable molecule and the surface, we anticipate the existence of more delocalized π-π interactions between the benzene rings and the Si dimers. We note that the angle between the line through the protusions and the silicon dimer rows has been found to be slightly smaller (20°) than for the stable state (30°). This results in a twisting of the phenyl ring relative to the silicon dimer such that the σ-σ valence bonds between C and Si atoms may not be facilitated. We emphasize that the switching of the bistable molecule between the two metastable configurations shown in Figs. 3(b) and 3(c) involves a large change of configuration. As a matter of fact, this switching can be thermally activated at room temperature through an energy barrier which has been estimated to be about 0.64 eV. The transformation of the bistable site into the fixed site involves an apparent change of geometry [from Figs. 3(b)–3(e)] which is much smaller. However, the binding of the molecule with the surface is believed to be very different in both cases, i.e., weak delocalized π-π interactions between the benzene rings and the Si dimers for the bistable site and stronger σ-σ valence bonds between C and Si atoms. Therefore, the energy barrier for the transformation of the bistable site into the fixed site may well be much higher than 0.64 eV.

In the stable state [see Fig. 3(e)], the benzene ring on top of the Si dimer has two C atoms which are above the positions of the Si atoms. One could then expect a bonding configuration through two C-Si (σ-σ) bonds very similar to the 1,4-cyclohexadiene-like structure of benzene adsorbed on Si(100).[15] We emphasize that the schematic diagrams in Figs. 3(b), 3(c), and 3(e) aim to indicate only the lateral positions of the phenyl rings with respect to the surface silicon dimers. However in the actual stable configurations, the phenyl rings may well be rotated with respect to each other along the molecular axis and the molecule may not be planar to the surface.

IV. CONCLUSION

In conclusion, we have shown that the room temperature adsorption of the biphenyl molecule on the Si(100) surface gives rise in majority to a bistable molecular configuration. At room temperature, the thermal energy activates the switching of the bistable molecule which appears as a striped site in the STM topography. STM manipulations enabled us to transform the bistable molecule into a fixed molecule or to desorb the bistable molecule. This demonstrates that the striped site is indeed a non dissociated biphenyl molecule adsorbed on the clean Si(100) surface without any defect. Low-temperature (30 K) STM topography enabled to freeze the bistable molecules in their equivalent stable states from which the adsorption geometry could be clearly identified. From the NEXAFS spectra, the bistable molecule appears to be chemisorbed through π-π interactions with the surface. The adsorption of biphenyl on Si(100) offers a unique opportunity for experimenting with a bistable molecule.

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