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Selective Scanning Tunnelling Microscope Electron-Induced Reactions of Single Biphenyl Molecules on a Si(100) Surface

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Abstract: Selective electron-induced reactions of individual biphenyl molecules adsorbed in their weakly chemisorbed configuration on a Si(100) surface are investigated by using the tip of a low-temperature (5 K) scanning tunnelling microscope (STM) as an atomic size source of electrons. Selected types of molecular reactions are produced, depending on the polarity of the surface voltage during STM excitation. At negative surface voltages, the biphenyl molecule diffuses across the surface in its weakly chemisorbed configuration. At positive surface voltages, different types of molecular reactions are activated, which involve the change of adsorption configuration from the weakly chemisorbed to the strongly chemisorbed bistable and quadristable configurations. Calculated reaction pathways of the molecular reactions on the silicon surface, using the nudge elastic band method, provide evidence that the observed selectivity as a function of the surface voltage polarity cannot be ascribed to different activation energies. These results, together with the measured threshold surface voltages and the calculated molecular electronic structures via density functional theory, suggest that the electron-induced molecular reactions are driven by selective electron detachment (oxidation) or attachment (reduction) processes.

1. Introduction

Over the past few years, a tremendous effort has been devoted to the design and fabrication of functionalized molecules. This includes molecules for molecular electronics, organic solar cells, organic light-emitting diodes, or nanomachines.[1−5] These molecules can be arranged in thick multilayers, monolayers, or self-assembled structures on surfaces for fabricating various devices. The ultimate miniaturization of devices down to the level of a single molecule requires being able to manipulate with precision individual molecules. Several techniques, such as nanogap junctions[6] and break junctions,[7,8] have been used in an effort to study electronic conduction through a single molecule. However, the contacts between the molecule and the electrodes are poorly defined, and there is increasing evidence that the configurations of molecular contacts need to be controlled with atomic-scale precision. The scanning tunnelling microscope (STM) has emerged as a powerful tool for such atomic-scale studies. It allows one not only to explore the structural and electronic properties of single molecules adsorbed on surfaces but, moreover, to activate their molecular dynamics through local direct contact,[9,10] vibrational excitation,[11−14] or electronic excitation.[15,16] This can be used to change at will their adsorption configuration and to test the functionality of each configuration.[17−29]

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If we compare STM manipulation of a single molecule by electronic excitation with STM manipulations by direct contact or vibrational excitation, electronic excitation has several advantages for inducing dynamical processes.[16,30] In particular, it should enable the molecule to be excited into far-from-equilibrium conformations, resulting in very rapid, efficient, and more controllable molecular dynamic processes.[16,30] A key problem is to demonstrate the selectivity of the electronic excitation, in particular of the polarity of the surface voltage during the STM manipulation. At positive surface voltages, tunnel electrons from the STM tip can be attached temporally to an unoccupied orbital of an adsorbed molecule, producing a negatively charged species (molecular reduction). At negative surface voltages, electrons can be temporally removed from an occupied molecular orbital, producing a positively charged species (molecular oxidation). As a result, one can expect very different molecular dynamical processes to be activated by positive and negative surface voltage STM manipulations.

In this paper, we report on the experimental and theoretical studies of the biphenyl molecule adsorbed on Si(100) in its weakly chemisorbed configuration. In this configuration, the biphenyl molecule has a unique behavior. Under STM-induced positive charging (oxidation), the molecule is shown to diffuse across the surface without any change of configuration. By reversing the polarity of the molecular charging from positive to negative values, various molecular reactions are activated, involving changes of adsorption configurations. It is then possible to transform a single biphenyl molecule from its weakly chemisorbed configuration to its strongly chemisorbed bistable or quadristable configurations. To understand the origin of the selectivity of these STM electron-induced molecular reactions as a function of the charging polarity, we have carried out calculations of (i) the electronic structure of the weakly chemisorbed configuration via density functional theory (DFT) and (ii) the energy profiles of the various molecular reaction pathways by using the nudge elastic band (NEB) method.[31]

2. Experiment and Theory

2.1. Experiment. Experiments are performed by using a low-temperature (5 K) ultrahigh vacuum (UHV) scanning tunnelling microscope (STM).[32,33] A clean Si(100) surface of a p-type B-doped silicon sample with a resistivity of 0.004−0.006 Ω cm is prepared in a UHV chamber as described elsewhere.[32,33] Biphenyl molecules are adsorbed on the Si(100) surface at a temperature below room temperature (~250 K) with a coverage of about 0.1 monolayer. Then, the sample is cooled down to 5 K and transferred into the low-temperature STM. All measurements are done with the voltage applied to the surface and the STM tip grounded.

2.2. Theory. The electronic structure calculations are performed using DFT within the generalized gradient approximation as implemented in the Vienna ab initio simulation program (VASP) code.[34] The electron−ion interaction is described by ultrasoft pseudopotentials (US-PP),[35] and the electronic wave functions are expanded by plane waves up to a kinetic energy of 350 eV. The reconstructed Si(100) surface is modeled by a periodically repeated slab of six silicon atom layers. The vacuum layer thickness exceeds 13 Å. The unit cell considered for the periodic calculations is the p(4 × 5) to account for low-coverage conditions (see the red rectangle in Figure 9). On the clean surface, the top silicon atoms give rise to 10 surface dimers per unit cell, while the dangling bonds at the bottom of the slab are saturated by hydrogen atoms. Brillouin zone integrations are performed using the γ-point. The uppermost two Si layers as well as the molecular degrees of freedom are allowed to relax until atomic forces are lower than 0.01 eV/Å.

A delicate step in this computational work is the minimization of the reaction pathways and the search of intermediate stationary points or saddle points connecting the phase spaces of reactant and product. These saddle points are thus the transition states (TS) of the reaction pathway. The climbing-image NEB[30] implemented in VASP has been systematically used to find these saddle points along the adiabatic minimal energy pathway connecting each initial and final state of a given elementary step. Finally, the TS states are identified by exhibiting the existence of a single normal mode associated with a pure imaginary frequency, the corresponding soft mode lying in the reaction coordinate.

An important part of this paper resides in the analysis of the biphenyl electronic structure in its initial adsorption configuration. A valuable tool is the projected density of states (PDOS) onto molecular orbitals recently used in a theoretical study of an STM-induced dehydrogenation of benzene and pyridine molecules on Cu.[36] Such PDOS provides information on the molecular character of the chemisorbed system. From this point of view, it is more interesting than the PDOS onto atomic orbitals used in many other works on molecular adsorption.

3. Results and Discussion

3.1. Weakly Chemisorbed Adsorption Configuration of Biphenyl Molecules on Si(100). The biphenyl molecule is made of two phenyl rings linked by a single C−C bond (Figure 1a). When adsorbed on the p-doped Si(100) surface at ~250 K, biphenyl molecules are known to be in their weakly chemisorbed configuration[37] (Figure 1a). The low-temperature (5 K) STM topography of Figure 1b shows several such biphenyl molecules. Enlarged topographies of a single biphenyl molecule recorded

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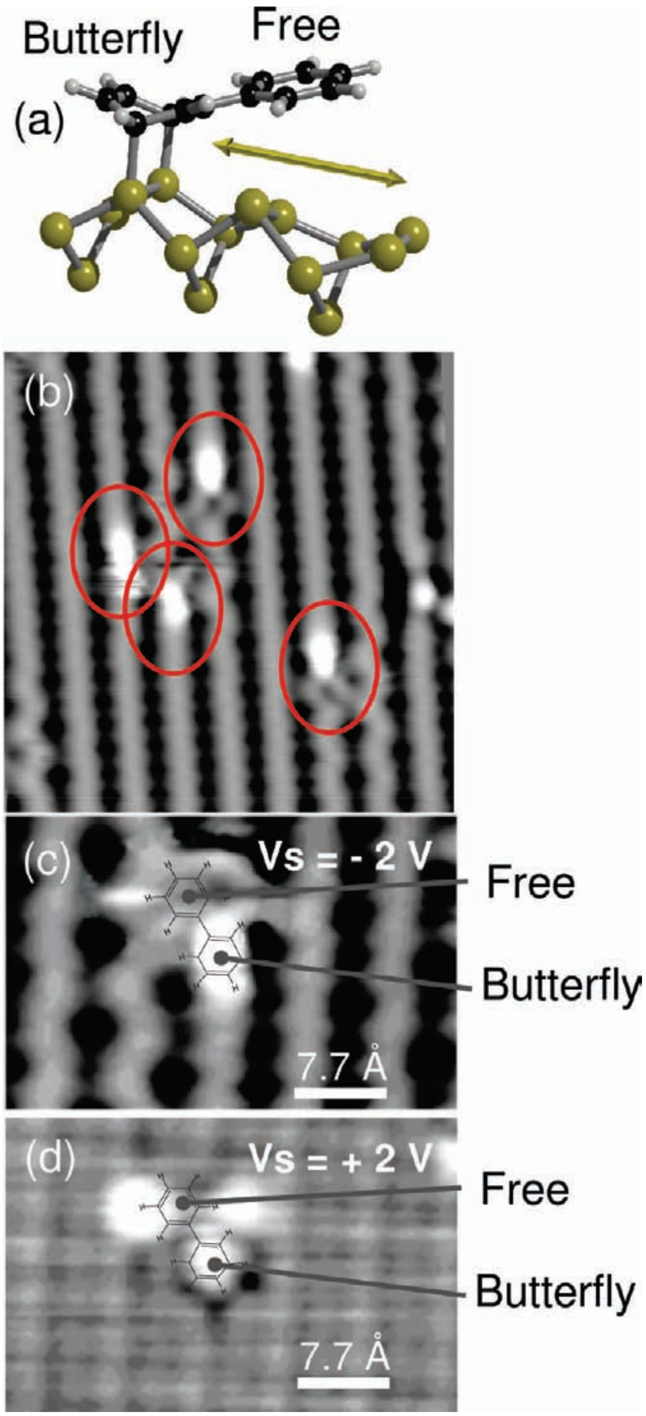

Figure 1. (a) Weakly chemisorbed adsorption configuration of a biphenyl molecule on the Si(100) surface. The butterfly phenyl ring of the molecule is bond to a silicon dimer through two Si−C bonds, whereas the free phenyl ring has no chemical bonding with the surface. The arrow indicates the direction of the silicon dimer rows on the 2 × 1 reconstructed Si(100) surface. (b) 7.0 × 7.1 nm^2 STM topography showing four weakly chemisorbed biphenyl molecules (circled in red) on the 2 × 1 reconstructed Si(100) surface. $V_S = -2$ V, $I = 240$ pA. The vertical gray lines are the silicon dimer rows. (c and d) a close-up of the STM topography over a single biphenyl molecule recorded with $I = 240$ pA and $V_S = -2$ V and $V_S = +2$ V, respectively. The free and butterfly phenyl rings of the molecule are indicated.

with a −2 V (occupied states) and a +2 V (unoccupied states) surface voltage are shown in parts c and d of Figure 1, respectively. The occupied state topography (Figure 1c) shows a bright feature centered on a silicon dimer row and a faint feature extending over three silicon dimer rows. The bright feature resembles that of the STM topography of the benzene molecule adsorbed on Si(100) in the so-called butterfly configuration recorded under similar surface voltage conditions.[38] In the butterfly configuration, the benzene phenyl ring loses its aromaticity and two opposite carbon atoms are bound to a silicon dimer through two Si−C bonds (see Figure 1a). Therefore, the bright feature in Figure 1c is assigned to one of the phenyl rings of the biphenyl molecule adsorbed in the butterfly configuration. The faint feature of Figure 1c is considered to correspond to the second phenyl ring of the biphenyl molecule free of any chemical bonding with the surface. The unoccupied state STM topography, shown in Figure 1d, is composed of three bright features. One of them is located at the same position as the bright feature in the occupied state topography. The two others are separated by more than 10 Å, which is more than the size of the biphenyl molecule (see Figure 1a). This cannot be assigned to any dissociation of the molecule since; as will be seen later, the same topography is maintained when the molecule diffuses across the surface. The two bright features separated by more than 10 Å are assigned to a weak electronic coupling between the silicon dimers and the free phenyl ring of the biphenyl molecule. In summary, the weakly chemisorbed configuration of biphenyl adsorbed on Si(100) shown in Figure 1a consists of one phenyl ring chemisorbed in the butterfly configuration and a second phenyl ring having no chemical bonding with the surface. The stability of this configuration has been previously demonstrated by DFT calculations.[39] We emphasize that this weakly chemisorbed configuration is markedly different from the previously studied, strongly chemisorbed bistable configuration,[39,40] where both phenyl rings are chemically bound to the surface (to be described later in this paper).

3.2. Diffusion of Biphenyl Molecules by STM Electron-Induced Manipulation with Negative Surface Voltage Pulses. The biphenyl molecules in the weakly chemisorbed configuration are very stable and are never observed to move during the STM topographies recorded under normal scanning conditions (surface voltage of −2 or +2 V with respect to the tip). However, the molecules can be diffused across the silicon surface by using the STM in its electron-induced manipulation mode as follows. After recording the STM topography of a biphenyl molecule, the STM tip is positioned on top of the center of the chemisorbed butterfly phenyl ring (Figure 2a), the feedback loop is switched off and a negative voltage $V_S < -3$ V is applied to the surface during a certain time (from 10 ms to 5 min). This time depends on the values of V_S and of the tunnel current. For each manipulation, the tip−surface distance d is adjusted to obtain the desired tunnel current. During the manipulation, the tunnel current is recorded as a function of time, as shown in Figure 2c. The abrupt decrease of the tunnel current indicates that the molecule has moved. This drop of tunnel current enables us to measure the time of excitation, t_{exc}. Afterward, a new STM topography is recorded to check that the molecule has moved (Figure 2b). A series of STM electron-induced molecular movements is shown in Figure 3. After each STM topography, a STM pulse with $V_S = -3$ V is applied to the molecule. As can be seen in Figure 3, various random translation movements,

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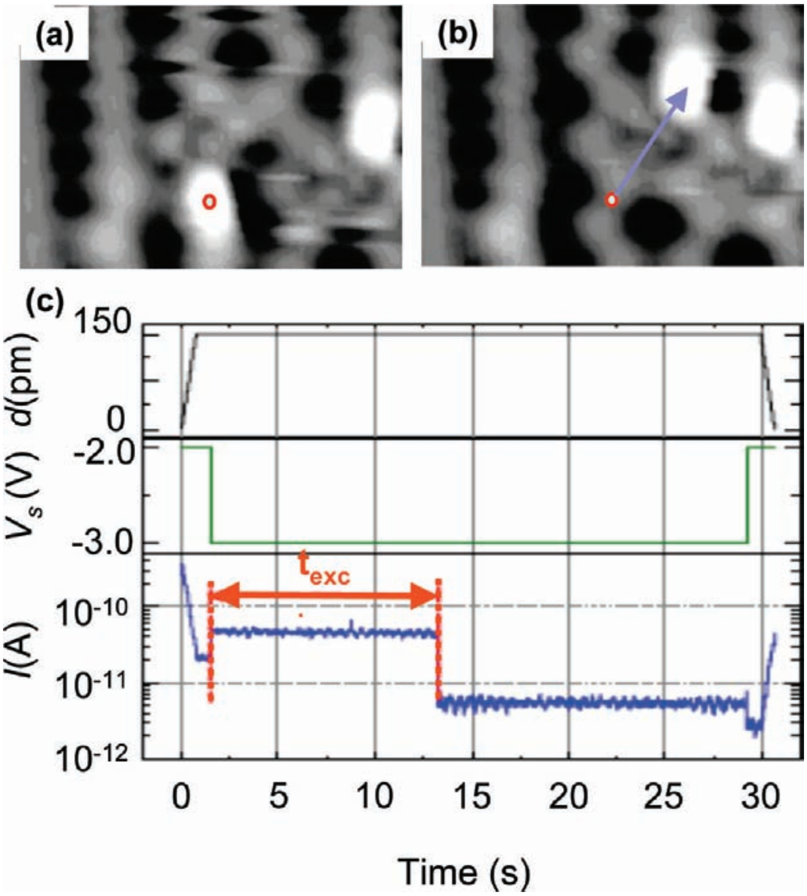

Figure 2. (a and b) STM topographies ($V_S = -2$ V, $I = 240$ pA) before and after the STM electron-induced diffusion of a biphenyl molecule. The initial position of the molecule is marked by a red circle. The blue arrow indicates the displacement of the molecule. Note that the second molecule has not moved. (c) Recorded STM tip−surface distance variation (d), surface voltage (V_S), and tunnel current (I) during the STM electron-induced manipulation. The STM tip−surface distance is increased by 150 pm and the surface voltage is increased to -3 V. The tunnel current trace indicates the time (t_{exc}) when the molecule diffuses across the surface.

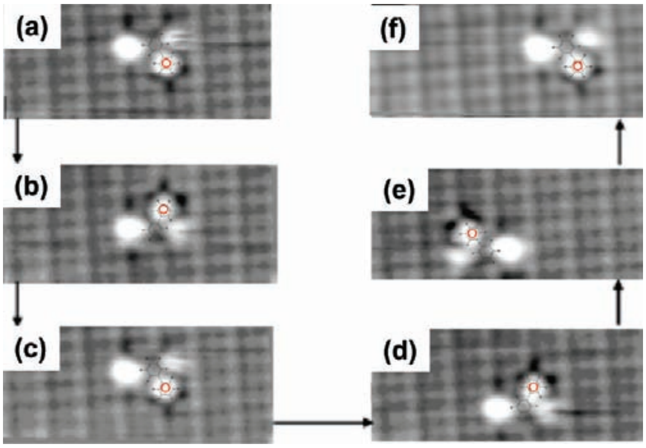

Figure 3. (a−f) A sequence of successive STM topographies (5.5 × 2.3 nm^2, $V_S = +2$ V, $I = 240$ pA) showing the diffusion of a single biphenyl molecule. The schematic drawing of the molecule is superimposed on each topography to indicate the position and orientation of the molecule. After each topography, a STM pulse ($V_S = -3$ V) is applied with the STM tip on top of the red dot.

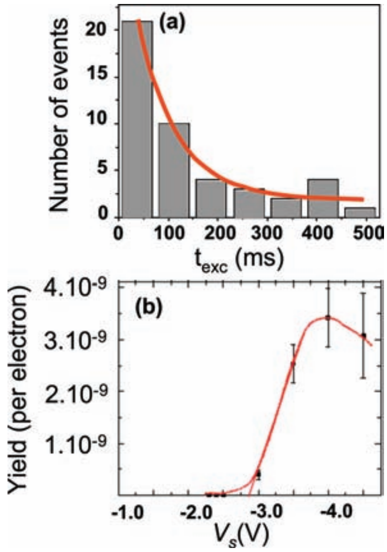

Figure 4. (a) Exponential distribution of the time of excitation t_{exc}. (b) Yield (per electron) as a function of the surface voltage for the diffusion of the biphenyl molecule.

accompanied by rotation, can be activated this way, resulting in the diffusion of the molecule across the surface without any change in the final adsorption configuration with respect to the initial one. For each value of V_S and tunnel current I, the distribution of t_{exc} is obtained by repeating the pulse and assembling the results in bins of fixed time over a large number of experiments[33] (Figure 4a). An exponential decay fit gives the average value τ of t_{exc}. The reaction yield, i.e., the probability per electron of activating the molecule diffusion, is obtained as

$Y_{\text{diff}} = 1/(I\tau/e)$.[33] For each value of V_S, the reaction yield is constant when varying the intensity of the tunnel current I from 50 pA to 1.3 nA. This indicates a one-electron process.[33] The reaction yield for diffusion Y_{diff} is shown as a function of the surface voltage V_S in Figure 4b. A threshold voltage of −2.7 ± 0.2 V is deduced by assuming a linear threshold law.[33] For all negative values of the surface voltage in the range from −2.3 to −4.5 V, the only observed reaction is the diffusion of the molecule across the surface in its weakly chemisorbed configuration. The observed threshold voltage at −2.7 V indicates that the diffusion is activated by a resonant transfer to the STM tip of an electron issued from an occupied molecular orbital located 2.7 eV below the sample Fermi level. This electron detachment creates a temporary positively charged molecular species equivalent to a transient oxidation of the biphenyl molecule.[33] Molecular dynamical processes induced by electron detachment (hole attachment) with the STM have been recently reviewed.[16] For molecules adsorbed on silicon, the processes are believed to be of the DIET (desorption induced by electronic transition) type.[16] Within the DIET model, the molecular ionization (oxidation) is rapidly followed by the capture of an electron from the silicon substrate and the subsequent return of the molecular system into its neutral electronic ground state. However, during this ionization−neutralization sequence, the molecular system has time to change its geometry. This change of geometry will then drive the observed molecular dynamics (e.g., diffusion).

3.3. Calculated Density of Electronic States and Diffusion Pathways of a Biphenyl Molecule in Its Weakly Chemisorbed Configuration. To understand the electronic processes inducing biphenyl diffusion, in particular the origin of the threshold voltage at −2.7 V, we have calculated the projected density of states (PDOS) of the biphenyl molecule in its weakly chemisorbed configuration (Figure 5a). The PDOS in Figure 5b have been obtained by projecting the DOS of the total system onto some molecular orbitals of the substrate-free biphenyl molecule depicted in Figure 5c. The width and shape of the various resonances indicate how the molecular states are coupled to the substrate in the adsorption configuration. The HOMO−2 and LUMO+2 orbitals, localized on the free phenyl ring, lead to narrow resonances, because they do not interact with the silicon surface. On the other hand, the HOMO−1, HOMO, LUMO, and LUMO+1 orbitals (that are spatially localized on the butterfly ring) are broadened due to strong coupling or hybridization with silicon states. The LUMO state shifts toward energies below the Fermi level, implying the back-donation of two electrons from the silicon to the molecule (an independent Bader charge analysis on this system confirms that the biphenyl molecule captures two electrons from the surface). From these data, it follows that ionization at −2.7 V can involve only π states of the molecule (mainly HOMO, HOMO−1, and HOMO−2). The removal of one electron from the HOMO or HOMO−1 orbitals, which are expected to have a strong molecule−substrate bonding character, should favor the desorption of the butterfly phenyl ring, i.e., the diffusion of the molecule.

The density of states (DOS) of the total system has been also projected onto the silicon atoms underneath the butterfly and the free phenyl ring of the biphenyl molecule (Figure 5d). The silicon atoms bonded to the butterfly phenyl ring have occupied DOS shifted 2.4 eV below the Fermi level, whereas the DOS of the silicon atoms below the free phenyl ring at −0.4 eV is unchanged as compared to the silicon atoms of the clean surface. This confirms that ionization at −2.7 eV involves orbitals localized at the silicon atoms linked to the butterfly phenyl ring.

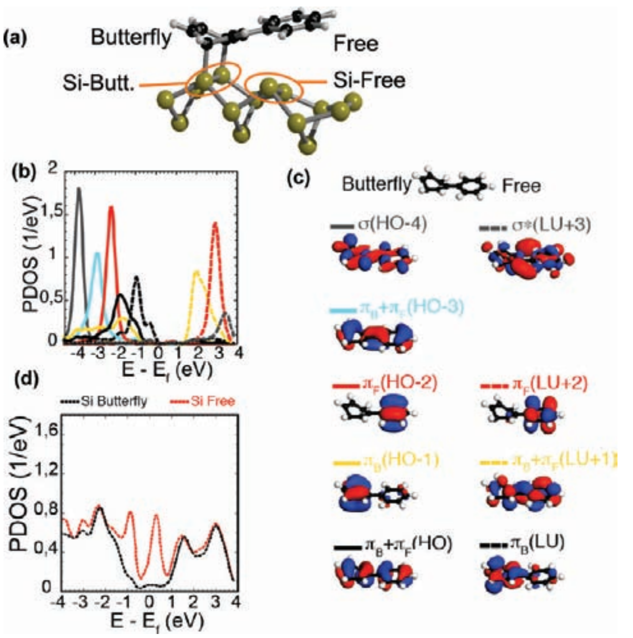

Figure 5. (a) Weakly chemisorbed adsorption configuration of a biphenyl molecule on the Si(100) surface. The silicon dimers underneath the butterfly phenyl ring (Si-Butt.) and the free phenyl ring (Si-Free) are circled in red. (b) PDOS of the weakly chemisorbed biphenyl on Si(100) onto the molecular orbitals of the substrate-free biphenyl. (c) Occupied (full lines) and unoccupied (dotted lines) molecular orbitals of the substrate-free biphenyl molecule with the conformation of the weakly chemisorbed biphenyl molecule. (d) PDOS of the weakly chemisorbed biphenyl on Si(100) onto the Si-Butt. and Si-Free silicon dimers.

To get insight into the diffusion of a biphenyl molecule in its weakly chemisorbed configuration, we have calculated the energy profiles of various diffusion pathways by using the NEB method described in section 2.2. Diffusion pathways involving either rotation of the biphenyl molecule (Figure 6) or translation along or across the silicon dimer rows (Figure 7) have been explored. Various metastable isomers of the adsorbed biphenyl have been identified and are sketched with top and side views in Figures 6 and 7. From these data, it appears that all the rotation and translation molecular movements have similar activation barrier energies around 0.8 eV. This nonselective diffusion is in good agreement with the experimental findings, since isotropic diffusion has been observed experimentally. We note that all the investigated diffusion pathways have transition states (TS) whose energy is very close to zero, i.e., to that of the desorbed biphenyl molecule. It follows that the TS structures can be viewed as weakly adsorbed species having loose bonds with the silicon surface. This physisorbed nature of the transition states is the key point to explain the isotropic diffusion of biphenyl molecules on the Si(100) surface whose atomic structure is known to be anisotropic.

In summary, diffusion of a biphenyl molecule in its weakly chemisorbed configuration has a barrier energy of 0.8 eV. In a single-electron STM manipulation process, overcoming this barrier energy requires a surface voltage lower than −0.8 V. The observation of a threshold voltage at a much lower voltage, i.e. −2.7 V, is explained by the fact that activating the diffusion requires ionization from π states (HOMO, HOMO−1) of biphenyl, whose energies are around −2.7 eV (see Figure 5b).

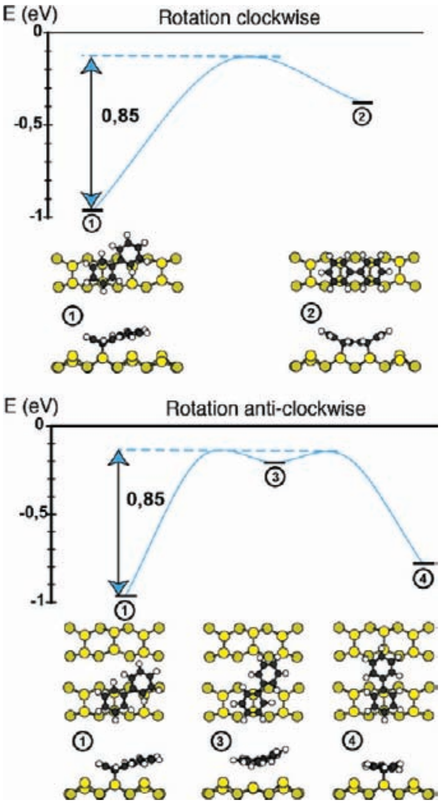

Figure 6. Calculated rotation pathways of the weakly chemisorbed biphenyl molecule on Si(100), either clockwise (top panel) or anticlockwise (bottom panel) around the surface normal axis. The 0 K energy profiles (in eV) are relative to the reference states made of the isolated biphenyl molecule and the bare silicon surface. Below each curve, the different conformations along the rotation pathways are sketched with top and side views.

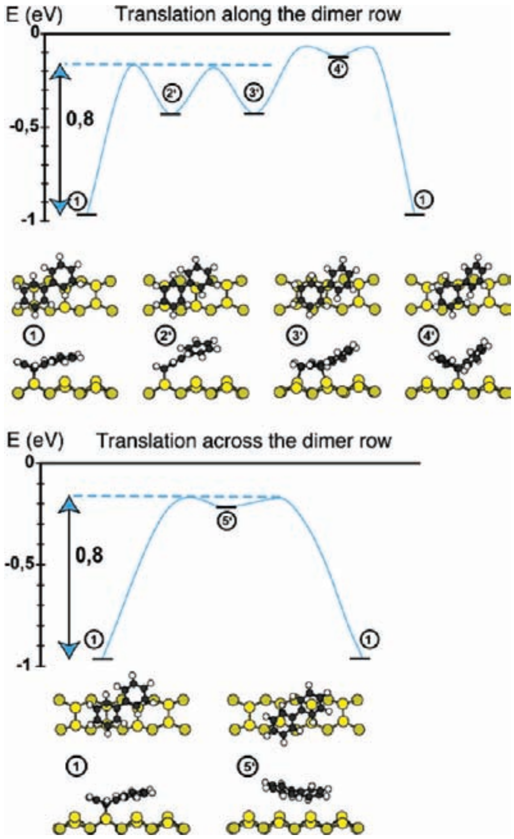

Figure 7. Calculated diffusion pathways of the weakly chemisorbed biphenyl molecule on Si(100). The biphenyl molecule translates laterally, either along the dimer row (top) or in the perpendicular direction (bottom), through activated processes into metastable isomers. The notations are the same as those of Figure 6.

3.4. Changes of Adsorption Configuration by STM Manipulation with Positive Surface Voltage Pulses. We have seen in section 3.2 that STM manipulation with negative surface voltage pulses induces diffusion of the molecule while it stays always in the same weakly chemisorbed configuration. On the contrary, STM manipulation with positive surface voltage pulses result in much more complex molecular reactions involving, in particular, changes of adsorption configuration. Experiments are performed using the same method as for negative surface voltage pulses. Since electron-induced reactions are found to be less efficient at positive surface voltage pulses, we use longer voltage pulses (4 s). Tunnel currents are about 1 nA and surface voltage pulses between +3 and +4 V. No reaction is observed for voltage pulses below +3 V. Several types of reactions can be induced with positive surface voltage pulses. The first one is the diffusion of the biphenyl molecule in its weakly chemisorbed configuration, as observed with negative voltage pulses. The second one is the change of adsorption configuration from its initial weakly chemisorbed configuration (W) to the strongly chemisorbed bistable configuration (S_1) (Figure 8a). The S1 bistable configuration, which has been previously studied in detail,[39] is recognized by its occupied state STM topography, where the two chemisorbed phenyl rings are seen as bright spots (Figure 8a). To ensure that the observed configuration is indeed the bistable one, the bistable movement of the molecule is activated several times by using negative (−3.5 V) surface voltage pulses, as was done in ref 33. This strongly chemisorbed bistable configuration (Figure 8a) is made of a mobile phenyl ring chemisorbed to the Si(100) surface through two Si−C bonds in the butterfly configuration and a fixed phenyl ring chemisorbed to the silicon surface through a single Si−C bond.[33,41] As a consequence of this latter Si−C bond formation, a hydrogen atom dissociated from the fixed phenyl ring is bound to the neighboring silicon atom of the same silicon dimer. The third type of electron-induced reaction is the change of adsorption configuration from the weakly chemisorbed configuration (W) to the strongly chemisorbed quadristable one (Q_1) (Figure 8b). The STM topography of the quadristable configuration is very similar to that of the bistable configuration. However, the quadristable configuration is easily recognized when exciting the molecule with negative pulses (−3.5 V), since it shows four different stable states instead of two for the bistable configuration.[42] As the four stable states of the quadristable configuration have the same probability to be produced by a negative pulse (−3.5 V), it is usually sufficient to perform a series of three pulses to distinguish the quadristable configuration from the bistable one. The quadristable configuration (Figure 8b) is a bistable configuration in which the hydrogen atom bound to the neighboring silicon atom is removed. As previously shown,[42] the removal of the hydrogen atom is sufficient to significantly modify the stability of the strongly chemisorbed configuration such that the resulting quadristable configuration has four stable states. The fourth type of electron-induced reaction is the change

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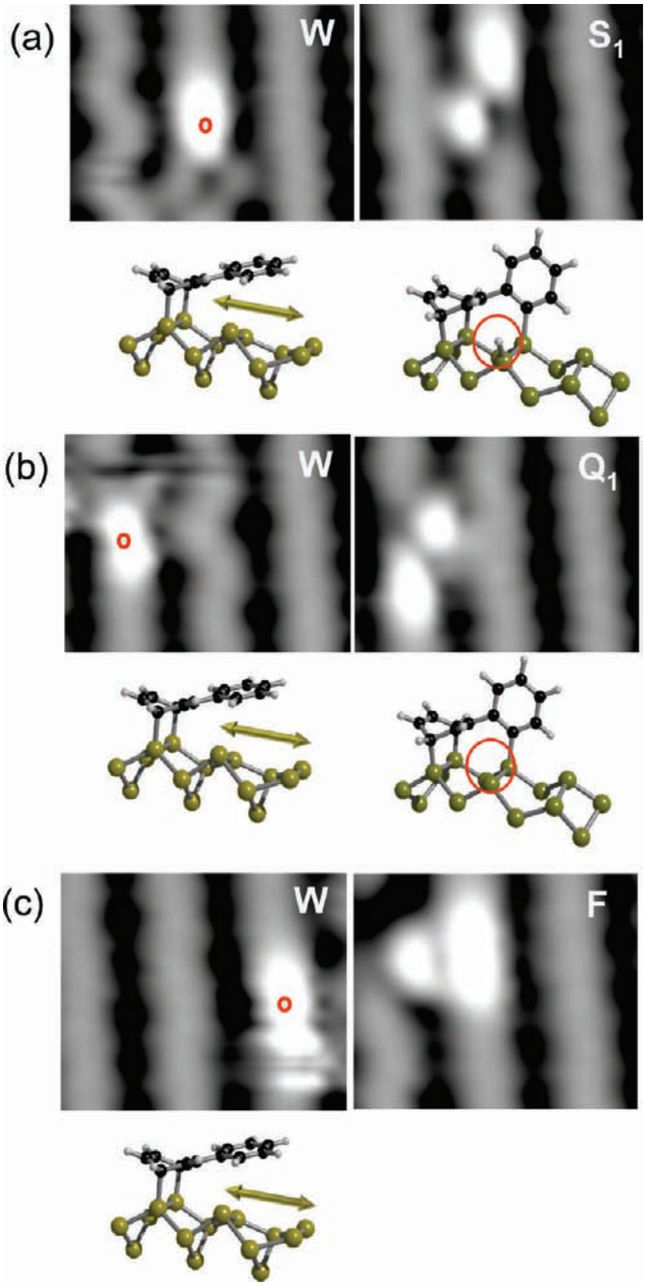

Figure 8. Changes of adsorption configuration by STM manipulation with positive surface voltage pulses. All 2.2 × 1.8 nm^2 STM topographies are recorded at $V_S = -2$ V and $I = 240$ pA. Left- and right-side STM topographies are recorded before and after STM manipulation, respectively. The red dots indicate the location of the STM tip during the surface voltage pulse at $V_S = +4$ V. (a) Change from the weakly chemisorbed (W) to the strongly chemisorbed bistable (S$_1$) configuration. (b) Change from the weakly chemisorbed (W) to the strongly chemisorbed quadristable (Q$_1$) configuration. (c) Change from the weakly chemisorbed (W) to the strongly chemisorbed fixed (F) configuration. The adsorption configuration of the biphenyl molecule is shown below each STM topography. For the S$_1$ configuration, the hydrogen atom dissociated from the fixed phenyl ring is circled in red. In the Q$_1$ configuration, the hydrogen atom has been desorbed.

of adsorption conformation from the weakly chemisorbed configuration (W) to the so-called fixed configuration (F) shown in Figure 8c. The fixed adsorption configuration is a very stable configuration, since the molecule in this configuration cannot be further moved by using negative surface voltage pulses. The F configuration in Figure 8c has not yet been identified with precision.

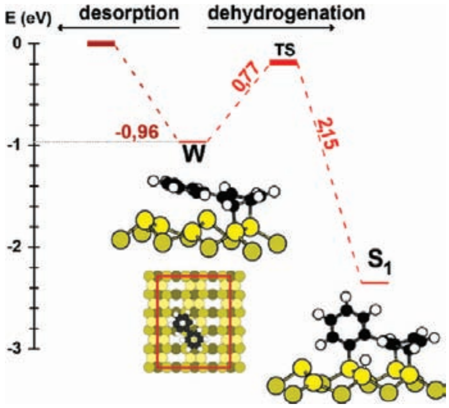

Figure 9. Calculated reactivity pathways of the weakly chemisorbed biphenyl molecule on Si(100) (W). The biphenyl molecule either desorbs (left) through a nonactivated process into biphenyl gas or dissociates (right) through an activated process associated with a transition state (TS) into the strongly chemisorbed bistable configuration (S$_1$). The 0 K energy profiles in eV are relative to the reference states being the isolated biphenyl molecule and the bare Si surface. The unit cell considered in the calculations is marked with a red rectangle on the top view of W. W and S$_1$ optimized structures are depicted with side zoom-in views.

Table 1. Probabilities for Various STM Electron-Induced Reactions of Individual Biphenyl Molecules on Si(100) as a Function of the Surface Pulse Voltage V_S

	probabilities for			
V_S (V)	diffusion	W → S$_1$	W → Q$_1$	W → F
+3.0	0.08	0	0.92	0
+3.5	0.40	0.13	0.43	0.03
+4.0	0.61	0.07	0.18	0.14

The probabilities for producing each type of reaction are reported in Table 1 as a function of the surface pulse voltage V_S. From the data in Table 1, we note a selectivity of molecular reactions as a function of the surface pulse voltage. At $V_S = +3$ V, reactions are dominated by a change of adsorption configuration from the weakly chemisorbed configuration (W) to the multistable configuration (M$_1$). On the contrary, at $V_S = +4$ V, the most probable reaction is the diffusion of the molecule.

The excitation processes associated with the positive surface voltage pulses are considered to be electronic processes involving the temporary attachment of electrons into unoccupied molecular orbitals.[16] Other effects such as electric field effects[16] are expected to be negligible. Indeed, during the surface voltage pulse, only the biphenyl molecule located just underneath the STM tip can react. Other neighboring molecules are never affected, even though they are located as close as 1 nm from the STM tip.

The striking result is that changes of configurations occur only at positive surface voltage pulses (attachment of electrons), whereas at negative surface voltage pulses (positive ionization) only diffusion of biphenyl molecules without any change of configuration can be activated. This can be understood from the PDOS calculations in Figure 5b. The unoccupied σ^*_{C-H} (LUMO+3) and π^*_{C-C} (LUMO+1 and LUMO+2) resonances have a pronounced C−H and C−C antibonding character, respectively. Positive surface voltage pulses from +3 to +4 V are expected to attach electrons to these σ^* and π^* states, thus leading to the excitation of C−H and C−C vibrations. Considering the intramolecular couplings between C−C and C−H vibrations, positive surface voltage pulses should then preferentially induce dissociation of C−H bonds, i.e., the change of adsorption configuration. On the contrary, as seen in section 3.3, negative surface voltage pulses involve the removal of electrons from π states (HOMO and HOMO−1 orbitals) which have a strong molecule−substrate bonding character. This should then favor the desorption of the butterfly phenyl ring, i.e., the diffusion of the molecule. This means that the observed selectivity of the molecular reactions as a function of the polarity of the surface voltage pulses can be explained by the bonding and antibonding characters of the involved molecular orbitals.

It is seen in Table 1 that diffusion of the molecule can also occur at positive surface voltage, especially at higher surface voltage (+4.0 V). This can be ascribed to vibronic intramolecular coupling, in particular when attaching one electron to the $\sigma^*_{\mathrm{C-H}}$ (LUMO+3) orbital, which is delocalized over the whole biphenyl molecule.

3.5. Changes of Adsorption Configuration; Calculated Pathways. Figure 9 shows the calculated energy profile for adsorption of a biphenyl molecule on Si(100) in its weakly chemisorbed (W) and strongly chemisorbed bistable (S_1) configurations. The desorption reaction from W is found to be a nonactivated process, since there is no transition state. The desorption barrier energy is 0.96 eV. We recall that the activation energy for diffusion in the W configuration has been found to be 0.8 eV (section 3.3). The change of adsorption configuration from W to S_1 involves the breaking of one C−H bond of the free phenyl ring of W and the creation of one Si−C bond and one Si−H bond on the same silicon dimer (see atomic structures in Figure 9). The activation energy for this reaction is found to be 0.8 eV. It follows that the diffusion of W across the surface and the W → S_1 change of configuration have very similar activation energies. Therefore, the observed selectivity of STM electron-induced surface reactions as a function of the surface voltage polarity cannot be ascribed to different activation energies of the various molecular reactions. This confirms that the observed selectivity relies on the different electronic structures of the various excited states produced when varying the surface voltage pulse from negative to positive values.

3.6. Calculated Conformational Pathways of the Bistable and Quadristable Configurations. As mentioned in section 3.4, the strongly chemisorbed bistable (S_1) and quadristable (Q_1) configurations, obtained after anchoring the weakly chemisorbed biphenyl molecule, are characterized by activating (with negative surface voltage pulses at $V_S = -3.5$ V) their reversible bistable and quadristable movements, respectively. Here, we have calculated the energy profiles of these bistable and quadristable movements in order to compare the dynamics of these strongly chemisorbed configurations with the dynamics of the weakly chemisorbed configuration discussed in sections 3.3 and 3.5.

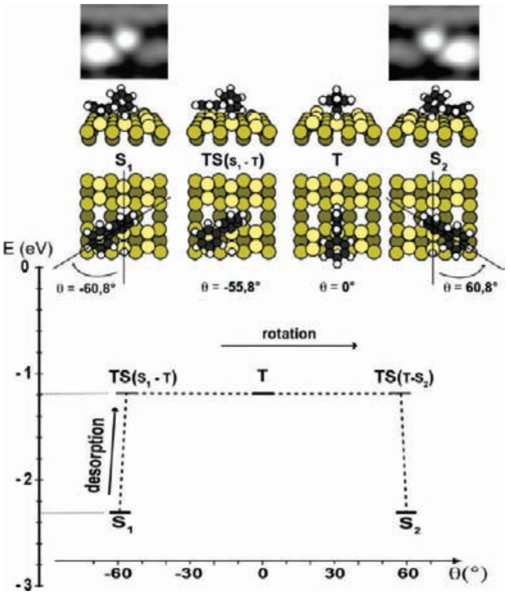

Figure 10. Calculated conformational pathways of the biphenyl molecule in its strongly chemisorbed bistable configuration (S_1). Some states along the pathways are shown with top and side views. The rotation angle θ corresponds to the angle between two perpendicular planes to the Si surface: one containing the upright dehydrogenated phenyl ring and one containg the Si dimer linked to H atom and the phenyl fragment. The TS structure corresponds to the desorption of the butterfly ring. STM topographies (1.7 × 1.5 nm^2, $V_S = -2$ V, $I = 240$ pA) of the biphenyl molecule in its S_1 and S_2 states are shown.

As shown in Figure 10, the movement of the biphenyl molecule in its strongly chemisorbed bistable configuration consists of a reversible rotation of the molecule from the S_1 stable state to the equivalent symmetric S_2 state. The rotation, around the fixed phenyl ring bonded to the surface through a Si−C bond, is defined by the angle θ (see Figure 10) equal to −60° and +60° when the molecule is in the S_1 and S_2 states, respectively. The mobile phenyl ring is bonded to a surface silicon dimer of the same dimer row through two Si−C bonds in the butterfly configuration.[33,41] The rotation movement requires breaking the two Si−C bonds of the mobile butterfly phenyl ring in the S_1 state, rotating the molecule from $\theta = -60°$ to $+60°$, and making two new Si−C bonds of the butterfly ring in the S_2 state. An unstable transient state (T) between the S_1 and S_2 states has been also evidenced in the experiments.[39] This T state is too unstable to be imaged with the STM. However, it could be directly observed between S_1 and S_2 by rapidly scanning the STM tip along a single line.[33] As shown in Figure 10, the activation energy of the bistable movement is relatively high (~1.2 eV). Once the butterfly phenyl ring of S_1 has been desorbed, it can freely rotate at constant energy to reach the transient state T and finally readsorb at the S_2 position. From our calculations, several shallow minima at about the same energy as the transition state (TS) and with barrier energies smaller than 0.05 eV are found between S_1 and S_2. For simplicity, these T transient states are represented by a single T state in Figure 10. The shallow minima explain the observed instability of the transient T states. The absence of any stable transient state is due to the presence of the hydrogen atom detached from the fixed phenyl ring, which passivates the silicon atom dangling bond underneath the transient state.[33] This prevents any attractive interaction between the mobile phenyl ring and the surface from occurring.

Figure 11 shows the calculated conformational pathway for the movement of the biphenyl molecule in its strongly chemisorbed quadristable configuration. This configuration is similar to the strongly chemisorbed bistable configuration, except that the hydrogen that passivated the silicon atom dangling bond underneath the fixed phenyl ring is now removed. Removing the hydrogen atom with the STM tip has been shown experimentally[42] to transform the bistable configuration into the quadristable configuration, which has four stable states (Q_1, Q_2, Q_3, and Q_4). In addition to the Q_1 and Q_2 stable states, which have geometries similar to those of the S_1 and S_2 states in Figure 10, two new metastable states are found at $\theta = \pm 11.6°$ and the $\theta = 0$ state becomes a transition state. These new metastable states Q_3 and Q_4 are stabilized by attractive interaction between the π electrons of the moving phenyl ring and the dehydroge-

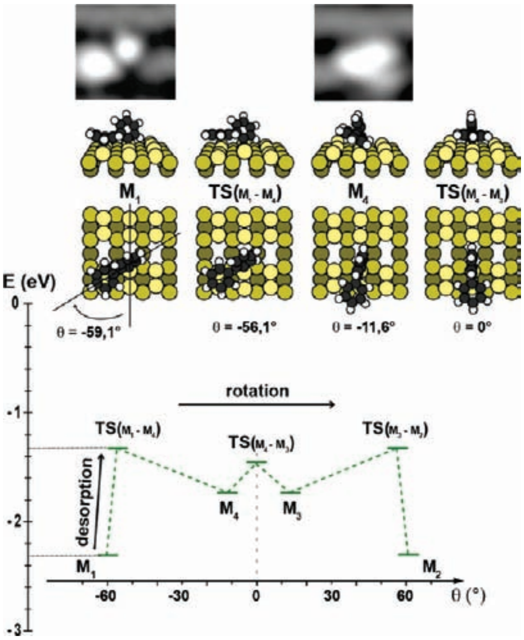

Figure 11. Calculated conformational pathways of the biphenyl molecule in its strongly chemisorbed quadristable configuration (Q_1). The notations are the same as those in Figure 10. This configuration has four stable states, Q_1−Q_4. STM topographies (1.4 × 1.3 nm^2, $V_S = -2$ V, $I = 240$ pA) of the biphenyl molecule in its Q_1 and Q_4 states are shown.

nated silicon dangling bond. These results explain well the observation of four stable states in the quadristable configuration.[42] Furthermore, the calculated activation energy for switching the quadristable molecule is found to be lower than for the bistable molecule (1.0 eV instead of 1.2 eV). This explains that the experimental switching efficiency of the quadristable configuration is increased by almost 2 orders of magnitude as compared to the bistable configuration.[42]

We emphasize that all the molecular reactions that have been investigated in this paper, i.e., diffusion of the weakly chemisorbed biphenyl, change of adsorption configuration from the weakly chemisorbed one to the strongly chemisorbed one, and switching of the bistable and quadristable configurations, have activation energies on the same order of magnitude in the range 0.8−1.2 eV. This corresponds to the energy required to break the two C−Si bonds of the butterfly phenyl ring.

4. Conclusion

By using a low-temperature (5 K) STM, we have investigated STM electron-induced reactions of single weakly chemisorbed biphenyl molecules on Si(100). Biphenyl on Si(100) appears as an ideal system for exploring in detail such STM electron-induced molecular dynamics, since it shows a large variety of molecular reactions that can be perfectly well-characterized both experimentally and theoretically.

Depending on the polarity of the surface voltage pulses during the STM electron excitation, very different molecular reactions are produced. At negative surface voltage pulses (e.g., −3.5 V), corresponding to transient molecular oxidation, the diffusion of the biphenyl molecule across the surface is the only observed reaction. At the same voltage intensity but with the positive polarity (+3.5 V), corresponding to transient molecular reduction, diffusion is still possible; however, the dominant reactions involve changes of adsorption configurations from the weakly chemisorbed to strongly chemisorbed (bistable and quadristable) configurations.

Calculated molecular reaction pathways using the nudge elastic band method enable a detailed description of these molecular reactions. In particular, they show that the molecular diffusion and the change of configuration from the weakly chemisorbed to the strongly chemisorbed configurations have very similar activation energies (∼0.8 eV). Therefore, the selectivity of the reactions with the voltage polarity cannot be ascribed solely to the sole energetic reasons.

Calculated projected densities of states show that this selectivity can be explained by the specific electronic structures of positively and negatively charged excited states of the weakly chemisorbed biphenyl on Si(100). The detachment of electrons (positive charging) from occupied π molecular resonances that have a molecule-surface bonding character activates the diffusion of the biphenyl molecules. On the contrary, the attachment of electrons (negative charging) to unoccupied π^* and σ^* resonances that have a strong intramolecular C−C and C−H antibonding character activates changes of molecular configuration.

These data point to a remarkable result; different molecular electronic structures of positively and negatively charged excited states are able to drive specific molecular reactions, even though the molecular reactions have similar activation energies. According to the DIET (dynamics induced by electronic transition) model, the observed molecular dynamics is a combination of dynamics in the excited and ground electronic states. The present results exemplify the importance of the dynamics in the electronically excited (charged) state. Despite a rapid relaxation (neutralization) to the ground electronic state due to the interaction between the molecule and the silicon surface, the molecular system is able to keep some memory of its specific electronic excitation. These data demonstrate that electronic excitation can be used to selectively power and control the dynamics of a single molecule adsorbed on a silicon surface. This opens interesting perspectives for the coherent control of molecular dynamics on surfaces,[43] for controlling the operation of molecular nanomachines,[5,16,44] or for activating selective surface chemistry.[45]

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