Conformational switching of single 1,5-cyclooctadiene molecules on Si(001) induced by inelastic electron tunneling

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A scanning tunneling microscope operated at 7 K is used to excite and probe the reversible switching of single 1,5-cyclooctadiene (COD) molecules on Si(001). Two different adsorption states are identified and attributed to the upright structure with only one C$=$C bond involved in the adsorption process and the bridge structure with both C$=$C bonds reacting with the Si surface. Time spectroscopy of the tunnel current with the tip positioned over the molecule in the bridge structure reveals a dynamic switching between two degenerate conformations, which is triggered by the vertical charge transport. In contrast, COD adsorbed in the upright structure gives rise to a binary switching response with an enhanced quantum yield and on-off ratio, along with nonequivalent current level mean residence times.

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The quest of continued device miniaturization requires new strategies to create electronic components at the nanometer scale. The molecular electronics approach[1] represents one such concept and aims at utilizing organic molecules as building blocks with predefined properties. In this context, the interaction of organic molecules with silicon surfaces gained considerable attention,[2] with the long-term goal of combining conventional semiconductors with new functionalities based on molecular structures linked to the semiconductor platform. A prototype functionality of interest is, for example, a bistable molecule that can be switched by an external stimulus. Such a behavior was recently observed by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), where single biphenyl molecules adsorbed on Si(001) were excited by inelastic electron tunneling (IET), leading to a reversible rotational movement of the molecule across the surface.[3] Further STM work[4] on styrene and cyclopentene on Si(001) revealed desorption, lateral molecular displacement, and adsorbate structural changes induced by IET. In this Rapid Communication, we present a case where cyclic alkene molecules on silicon undergo a reversible binary switching in an STM tunnel junction, which is ascribed to internal conformational switching of the molecule without any bond breaking effects involved. It is found that the tunnel current noise signature systematically and sensitively depends on the set point parameters of the tunnel junction as well as on the atomic-scale adsorption structure of the molecule.

In the present experiment, we used an ultrahigh vacuum (UHV) low-temperature STM operated at 7 K and studied the adsorption and tip-induced switching of single 1,5-cyclooctadiene (COD) molecules on a Si(001) template. As a free molecule, the eight-carbon cyclic alkene COD exists in two degenerate ground state conformations of chiral symmetry known as the "twisted-boat" form.[5] When adsorbed on Si(001), Hamers *et al.*[6] found that the molecule binds via [2+2] cycloaddition between the π bond of the unsaturated hydrocarbon and the dangling bonds of a Si dimer of the reconstructed surface. The actual COD/Si(001) adsorption geometry is as yet under debate: While Hamers and co-workers[6,7] concluded from experiments in the monolayer

coverage regime that COD adsorbs in the upright structure (one of the two π bonds reacts with a Si dimer), density functional theory (DFT) calculations[8] indicated that the bridge structure (both π bonds react with two adjacent Si dimers) is the most stable adsorption geometry. This controversy was also discussed in depth in a review by Wolkow.[2] Our data reveal that, in fact, both geometries occur at low coverage (here about 10^{13} molecules/cm^2, equivalent to 3% of the Si dimer surface density) with the bridge structure as the prevalent structure. The present system is a promising candidate to induce and probe a controllable single-molecule switching behavior because it implies a well defined covalent surface linking of the molecule via cycloaddition[6] as well as an intrinsic conformational bistability.[5]

n-type Si(001) samples [As doped, <0.01 Ω cm] were degassed in UHV at 850 K for several hours followed by flashing to 1300 K to remove the protective oxide. Prior to UHV treatment, the samples were chemically etched and reoxidized by the sulfuric acid/peroxide method described in Ref. 9. COD (Aldrich, 99+% purity) was adsorbed in UHV by dosing through a leak valve for 10 s at about 5×10^{-7} Pa and at room temperature followed by sample cooling to 7 K. We used electrochemically etched W tips cleaned in UHV by electron beam heating. In the experiment, the STM tip condition was checked by recording the differential tunneling conductance dI/dV (as a measure of the local density of states) of the bare Si(001) surface. Consistent with previous STS work,[10,11] the reference measurements confirmed a surface band gap of about 0.7 eV as well as spectral peaks at -1.0, $+0.3$, and $+1.0$ eV relative to the Fermi level, which are attributed to the π and π^* surface states, and the Si backbond states, respectively.

Figure 1(a) shows a filled-state image of the Si(001) surface [240×160 Å^2, -2 V] after the adsorption of COD molecules: The Si dimer rows run vertically, showing residual defects in terms of missing dimers[12] (imaged as depressions) along with two types of protrusions labeled as A and B on top of the rows that correspond to two different states of the adsorbed molecules. Figures 1(b)–1(d) detail the imaging of the adsorption states A and B at different sample bias relative to the tip. The molecule in state A is imaged as a uniform
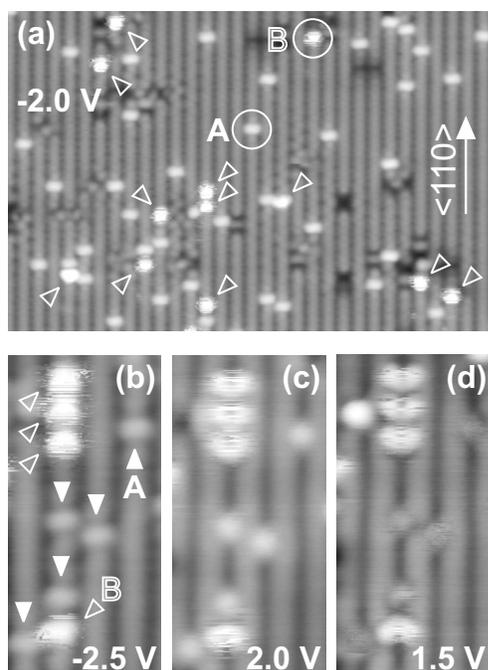
FIG. 1. (a) Constant-current STM image (240×160 Å^2, 1 nA, -2 V) of Si(001) taken at 7 K after COD dosage at room temperature: two different adsorption states labeled as A and B are observed along with residual surface defects in terms of missing Si dimers imaged as depressions. The lower panel details images (33×69 Å^2, 0.1 nA) of species A and B taken at (b) -2.5 V, (c) $+2.0$ V, and (d) $+1.5$ V.

FIG. 2. (Color) Color-coded STM image (106×80 Å^2, 0.6 nA, -2 V) of a Si(001) surface terrace with seven A-type COD molecules, see the protrusions depicted in magenta (a); the inset (30×20 Å^2) shows the Si dimer buckling at the upper step edge serving as a marker for the dimer positions within a row (see grid lines). The lower panel (b) illustrates the structure of one of the two possible conformers of COD adsorbed in the bridge structure (sphere model according to Ref. 8).

protrusion (height <0.6 Å), except for bias voltages close to the valence band edge (-1 V, not shown in Fig. 1) where it appears as a depression. The molecule in state B, on the other hand, has an increased apparent height as compared to A and an enhanced tendency to fluctuate during constant-current imaging (to a smaller extent, fluctuations during imaging are also observed for molecules in state A; they become more obvious in the time spectroscopy measurements discussed below). While a B-type molecule is imaged as a single-lobe protrusion centered on top of the dimer row at negative bias [filled states, Fig. 1(b)], it converts to a V-shaped double lobe structure at positive bias [empty states, Figs. 1(c) and 1(d)]. Note also that an upstanding V shape is found for the three B-type molecules in the top part of the images in Figs. 1(c) and 1(d), while the B-type molecule at the bottom appears to be rotated by 180° to yield an upside down V shape.

The uniform protrusions induced by molecules in state A are always centered between two adjacent Si dimers. We interpret this observation as an indication that the prevalent adsorption state A corresponds to the bridge structure [see the related sphere model in Fig. 2(b) based on the DFT calculations by Cho *et al.*[8]]. The site determination procedure is illustrated in Fig. 2(a): The Si dimer buckling[13,14] pinned by a monatomic surface step [see upper part of the color-coded image showing a Si(001) terrace with seven A-type molecules] is used as a marker for the positions of Si dimers within a row (see inset). As evident, each protrusion induced
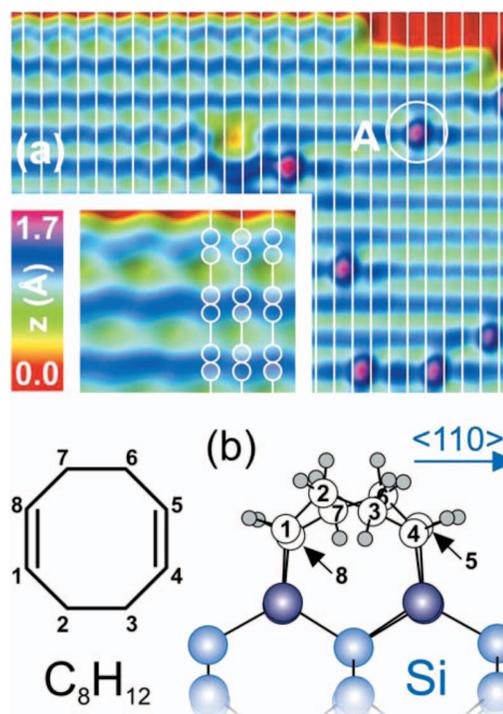
by a molecule (shown in magenta) is located in between the grid lines marking the dimer positions.

Time spectroscopy of the tunnel current with the feedback loop turned off and the STM tip positioned at a fixed distance over the molecule adsorbed in the bridge structure reveals a random telegraph signal, i.e., fluctuations between two levels of current with an on-off ratio of about 1.2:1. Higher tunnel currents (due to an increased sample bias and/or a decreased tip-to-surface distance) result in higher switching rates. This is exemplified by the data in Fig. 3, showing the telegraph noise recorded [Fig. 3(a)] at constant tip height (set point current and bias: 150 pA, 2 V) for different bias voltages and [Fig. 3(b)] at a constant bias of 2.5 V with a successive reduction in tip height starting from a set point of 25 pA and 2 V. The statistical evaluation of the binary current response shown in Fig. 3(c) reveals an exponential decay of the residence times of the random telegraph noise in the [Fig. 3(d)] high- and [Fig. 3(e)] low-current states, yielding essentially the same mean residence time τ for both states.

Figure 3(f) summarizes the switching rate $R = 1/\tau$ measured as a function of the mean current at various bias voltages and set point parameters. The data were obtained with different tips for different samples and during different experimental runs, thus demonstrating that the noise characteristics is a generic property of the COD molecules on Si(001).
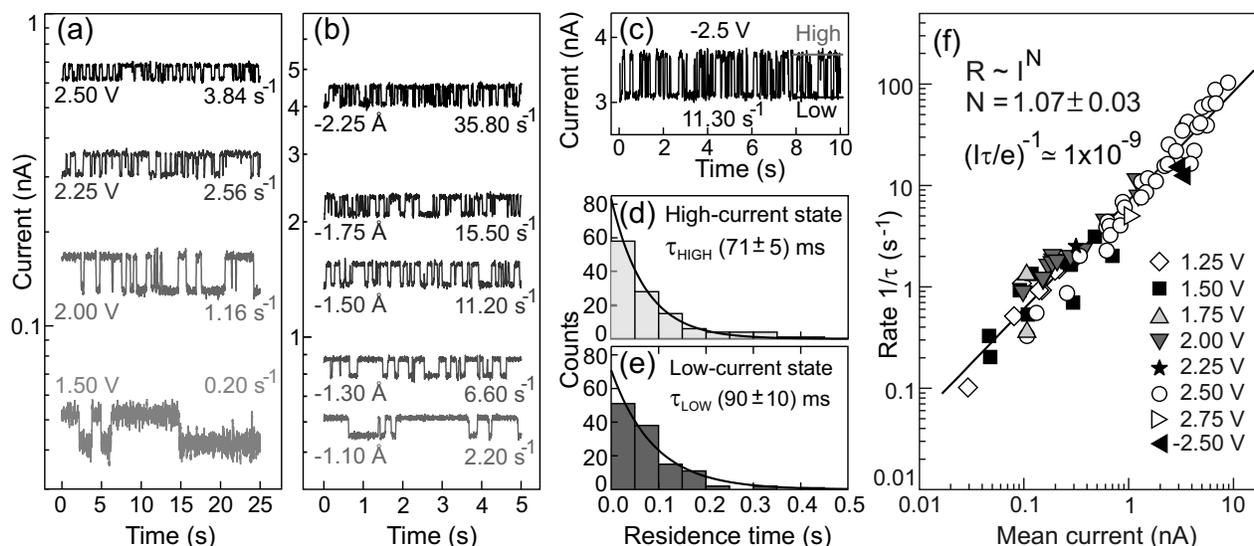
FIG. 3. Binary current fluctuations detected when tunneling through the A-type molecule (bridge structure) at (a) constant tip height (set point 150 pA, +2 V) and varying bias as well as at (b) a constant bias of +2.5 V and varying tip height [starting at a set point of 25 pA and +2 V]; the switching rate obtained for each current trace is indicated. Statistical evaluation of the exemplary current trace in (c) taken at −2.5 V bias, yielding an exponential distribution of the particular residence times in the high (d) and the low current state (e) with essentially the same mean residence times in both states. The switching rate R measured at various bias voltages and set point parameters [see (f)] depends linearly on the mean tunnel current with a slope close to 1, indicating that a single-electron excitation process triggers the switching. All time-dependent current measurements were performed with the feedback loop turned off.

Care was taken to address A-type molecules which were separated from adjacent molecules and surface defects. In the double logarithmic representation, the observed trend is well described by a linear current dependence with a slope of one so that $R \sim I^N$, with $N = 1.07 \pm 0.03$, suggesting that the molecular switching is triggered by an inelastic single-electron process.[15] The R versus I power-law dependence, with N close to 1, implies a constant quantum yield of $(I\tau/e)^{-1} \approx 1 \times 10^{-9}$ at the investigated bias voltages plotted in Fig. 3(f) [i.e., 150 pA switch the molecule about once a second on average]. The observed "Morse key" response to the vertical charge transport is obviously due to a IET-induced dynamic switching between two equivalent conformational states of the adsorbed molecule. The existence of two degenerate conformations of the COD molecule when adsorbed on Si(001) in the bridge structure was also predicted by DFT calculations.[8]

We now turn to the adsorption state B, which occurs less frequently than the bridge structure. The increased height in constant-current imaging and the enhanced sensitivity to tip-induced fluctuations suggest that this state corresponds to the upright structure. Molecules in state B are often (but not always) found in proximity to other equivalent molecules [see the groups of two and three B-type molecules in Figs. 4(a) and 1(b)–1(d)] or close to surface defects such as dimer vacancies. This observation is consistent with arguments stated in earlier work[2,8] that the energetically less favorable upright structure may exist due to surface defect-mediated rebonding as well as steric effects. Figure 4 illustrates that the upright COD/Si(001) structure is characterized by a clearly different response to STM tip-induced excitation: When positioning the STM tip over a B-type molecule as

indicated by the cross in the constant-current image in (a), a telegraph noise signal with an enhanced quantum yield (about 5×10^{-8}), a larger on-off ratio (about 2:1), and a non-equivalence in the current level population probabilities is observed. For B-type molecules, we find a sensitive dependency of the actual current noise signature on the lateral tip position. This increased complexity in fluctuation behavior is
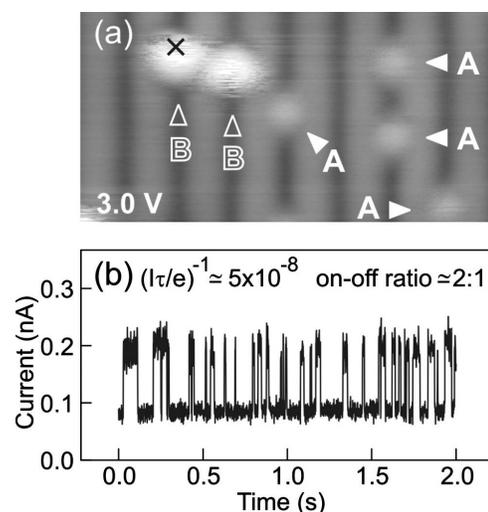

FIG. 4. (a) STM image (58×29 Å^2, 0.1 nA, 3 V) of two adjacent B-type molecules (upright structure); the black cross indicates the tip position at which the tunnel current trace shown in (b) was detected at a bias of +2 V (set point prior to opening the feedback loop: 0.1 nA, 3 V), indicating a significant enhancement of the quantum yield and the on-off ratio.

reasonable considering that more internal degrees of freedom are expected to exist for a COD molecule in the single Si dimer-bound upright structure compared to the bridge structure where the molecule is linked by both $C=C$ bonds to two adjacent Si dimers. While further experiments are required to explore the complex switching response of the B-type COD/Si(001) molecule in detail, the data in Fig. 4 support the assignment to the upright structure and clearly demonstrate the subtle dependency of the IET-induced molecular fluctuations on the adsorption state.

Finally, the present experimental findings on the STM imaging of COD/Si(001) molecules are discussed in comparison to earlier theoretical results. Cho *et al.*[8] reported simulated filled-state images of the upright and bridge structures at a tip height of 3 Å. Their bridge structure appears as a double-spot feature originating from the outermost $C—H$ bonds involving the C atoms 2 and 6 indicated in the sphere model of the conformer shown in Fig. 2(b), or alternatively, the C atoms 3 and 7 in the case of the other conformer (not shown). Our results do not provide evidence for a double-spot feature. We estimate the tip height in the present experiment to be larger by at least a factor of 2 compared to that assumed in the simulations. This larger tip height (washing out the charge corrugation) may be a potential reason for this discrepancy. For the upright structure, the simulations yield a single-spot feature, which was attributed to the bonding π orbital of the unreacted $C=C$ bond. This appearance is consistent with the experimental result in Fig. 1(b). No simulated images are available for the empty-states regime, where a double-lobe structure is observed for the upright structure

with the nodal plane parallel to the dimer row direction [see Figs. 1(c) and 1(d)]. We interpret this appearance as a signature of the antibonding π^* orbital of the unreacted $C=C$ bond reaching out into the vacuum region.

In summary, the present low-temperature STM observations indicate that single COD molecules adopt both the upright and the bridge structures upon adsorption on Si(001). While the bridge structure represents the prevalent and energetically[8] favorable configuration, the formation of the upright structure is likely to be promoted by the bonding to defects and steric effects. For the bridge structure, a reversible switching between the two energetically degenerate conformers is observed upon vertical charge transport through the molecule. This behavior is attributed to inelastic single-electron excitation in the situation of an adsorbed bistable molecule characterized by a double-minimum potential energy surface. A significantly different and more complex switching response is observed for the upright structure, which is due to the larger extent of internal degrees of freedom of the molecule in this adsorption geometry. Our results highlight a reversible switching scenario which is due to an internal conformational conversion of a single molecule without any bond breaking and rebonding. Future experiments will also focus on proximity effects, i.e., the role of collective phenomena such as molecule-molecule interactions in the switching behavior.

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