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Switching the Chirality of Single Adsorbate Complexes**

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The adsorption of achiral molecules on achiral surfaces often leads to chiral adsorbates.[1,2] In principle, a single molecule may create a chiral motif on the surface, if it belongs to the C_{nh}, C_s, or Ci point groups.[3] Either handedness results, depending on which enantiotopic side faces the surface. The breaking of mirror symmetry is also induced by the chiral distortion of the molecular frame, because of different distances of atoms to the surface, or by supramolecular and substrate lattice-induced chiral arrangements.[4] These chirality-inducing processes have in common that in the absence of additional enantioselective influences both enantiomeric states form at the surface, producing a racemic mixture.

Adsorbate motions are the most fundamental steps in surface chemistry.[5] In particular when collisions with other reaction partners or reactive surface sites are required, adsorbate motions are typically the rate-determining steps of a heterogeneously catalyzed reaction. Studying the movement of adsorbates, induced by phonons, photons, or electrons, is therefore of paramount interest. The role of vibrational molecular modes for the process of adsorption has been investigated in much greater detail than those involved in lateral motion on a surface. An important question here is how the vibronic excitation of a molecule couples to the lateral translation across the surface and which state-resolved excitations lead preferentially to lateral movement or other actions, like rotation, dissociation, or desorption.

Scanning tunneling microscopy (STM) has developed into more than an imaging tool, and the manipulation of single atoms and molecules with the STM tip is a well-established procedure.[6] Previous applications include the positioning of atoms into artificial structures[7] and even the lateral separation of enantiomers.[1d] The excitation of molecular vibrations by means of inelastically scattered tunneling electrons from the tip of the STM can lead to various dynamical processes at surfaces, such as molecular desorption,[8] dissociation,[9,10] formation of chemical bonds,[10] changes in conformation,[11] and rotation or hopping of molecules.[12] STM was also used to get insights into various aspects of chirality at surfaces, including intermolecular chirality recognition and transfer,[13] two-dimensional separation of enantiomers,[14] and chiral amplification.[15] Here we show that the two distinct enantiomeric states of a chiral single adsorbate can be interconverted by inelastic electron tunneling (IET). The prochiral molecule propene (C_3H_6) first forms a chiral adsorbate on a copper(211) surface. The absolute configuration of the adsorbate complex is then switched under the STM tip by IET into the opposite configuration. A process that goes beyond the IET-induced adsorbate motions that have been reported previously.[6,8–12] In order to better understand the molecular dynamics of chirality switching, we also describe related IET-induced adsorbate actions, like rotation and translation.

After adsorption of propene at 40 K on the intrinsically stepped Cu(211) surface under ultrahigh-vacuum conditions, two types of species are observed, each occurring in two enantiomeric states (Figure 1). The Cu(211) surface consists of (111) terraces separated by (100) single steps (see Figure S1 in the Supporting Information). Consequently its STM image

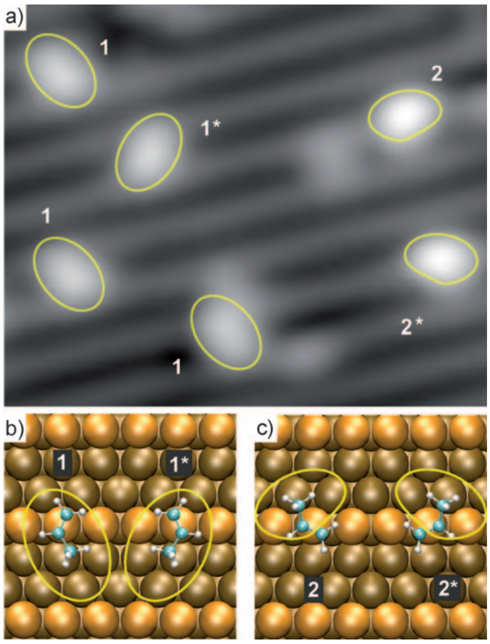

Figure 1. a) STM image (6.1 nm×4.9 nm, $T=7$ K) of propene on Cu(211). The intrinsically stepped surface appears as dark and bright stripes, the latter located near the step edges. Two species of adsorbates (**1**, **2**) are observed, both appearing in two mirror-related states (**1**,**1*** and **2**, **2***). b,c) Lowest energy configurations as obtained from DFT calculations. The methyl group dominates the STM contrast; for species **1** there is a contribution from the C=C bond.

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is dominated by dark and bright stripes, the latter located on the terrace near the step edge.[16] Propene molecules of type **1**, which are much more abundant, appear as elliptically shaped protrusions, whereby their centers are located at intrinsic step edges (Figure 1 a). Handedness is expressed by the tilt of the long molecular axis either to the left or the right with respect to [$\bar{1}$11], that is, the direction in the surface plane running perpendicular to the step edges. Molecules of type **2** generate brighter spots located on the bright stripes of the substrate. The elliptical shape with a small protrusion is rotated either to the right or to the left. DFT calculations reveal that in both adsorbate types the molecules are bound with the $C{=}C$ bond on top of a copper atom of the step edges; the methyl group either points towards the lower terrace (**1**,**1***) or the methyl group is located at the upper terrace (**2**,**2***; Figure 1). Side views of these adsorption geometries and the adsorption-induced charge difference are shown in Figures S2 and S3 in the Supporting Information. The methyl group dominates the STM contrast in **2**, because it points up. In **1**, the methyl group is not as dominant because the $C{=}C$ bond contributes substantially to the STM contrast.

The propene/Cu(211) adsorbate system thus exists in two rotamer states, each of which also appears in two enantiomeric states (**1**,**1*** and **2**,**2***). The difference in binding energies, as obtained by DFT, amounts to 50 meV.[17] The two rotamer states can be interconverted by IET (Figure 2 a,b). The procedures to induce a molecular response with IET have been described previously:[12,18] After imaging the target molecule at an initial position and orientation, the STM tip is positioned over the molecule. The tunneling current is recorded as a function of time at a fixed bias voltage. A jump in current indicates then that motion has occurred, and rescanning of the same area reveals the nature of the action. From the residence time until motion, the rate of that molecular action is deduced (see Figure S4 in the Supporting information). Plotting the reaction yield per electron as a function of sample bias at chosen tunnel current gives the IET action spectrum (Figure 2 c).[19]

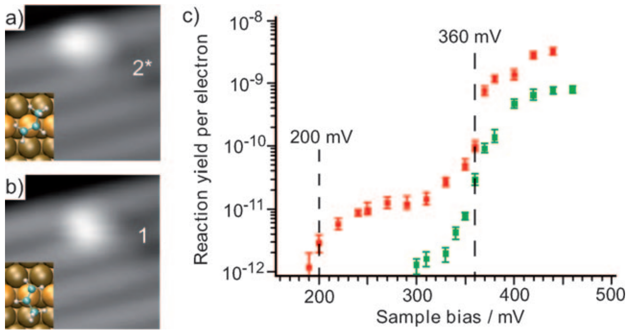

Figure 2. IET-induced rotation. a,b) STM images (3 nm × 3 nm) of the same propene molecule before (a) and after (b) IET-induced rotation ($V_s = 320$ mV, $I = 2$ nA for 2 s). c) IET action spectra for forth (**2*** → **1**; red squares) and back rotation (**1** → **2***; green squares). The threshold voltages at 200 mV and 360 mV correspond to the vibrational excitation of the stretching modes $\nu(C{=}C)$ and $\nu_s(CH_3)$ (see Table T1 in the Supporting Information).

The rotamer **2*** (or **2**) can be transferred to **1** (or **1***) and back. The conversion between the two rotamer states strongly depends on the bias voltage applied between the tip and the sample. That is, above a certain threshold bias the rate of conversion increases exponentially (Figure 2 c). The threshold bias, in turn, can be correlated directly to a molecular vibration.[19] The conversion of **2*** into **1** requires a bias voltage of about 200 mV (Figure 2 c) and correlates with the $C{=}C$ stretching vibration at 204 meV (see Table T1 in the Supporting Information).[20] Interestingly, the back rotation requires a much higher bias voltage, which is related to the CH_3 stretching vibration. Therefore, the coupling of the $C{=}C$ vibration to the rotation mode depends on the starting configuration. This motion mode cannot couple to the excited $C{=}C$ vibration in **1**. The correlation of the tunneling current and the motion probability can be used to deduce the reaction order. The rate R of a particular action is proportional to the electron current I and the number of electrons involved N: $R \propto I^N$.[19] As the slope of the $\lg R$–$\lg I$ plot for the rotation by IET manipulation is 1 (see Figure S4 in the Supporting Information Figure S4), the process is of first order with respect to the electrons.

A further increase in bias voltage allows excitation of the three $C(sp^2)$–H stretching vibrations. One of these high-frequency modes couples to a translation mode on the surface and vibration-induced translation is observed (Figure 3). This hopping is constrained along the step edge. The energy stored in that mode by a tunneling electron must be higher than the diffusion barrier to the next Cu atom on a step edge. The intermode energy transfer by anharmonic coupling of the molecular stretching vibration to the translation mode induces the movement.[19d] Which of the three $C(sp^2)$–H stretching vibrations is involved in this motion cannot be concluded because of the limited resolution of the IET action spectroscopy. However, the movement direction along the step edge coincides with the direction of the C–H bond in the DFT-based structure model (Figure 1 b). This suggests that the excited single C–H stretching mode at the sp^2-hybridized carbon atom is the one that couples to the translation mode.

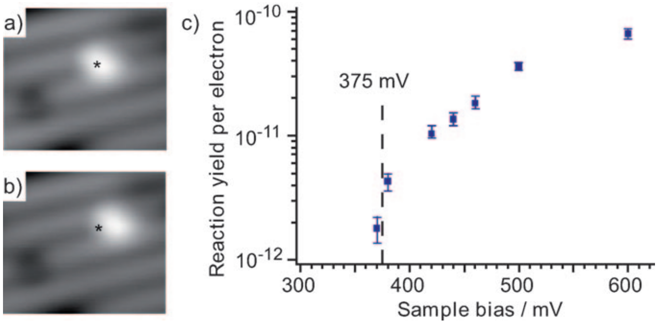

Figure 3. IET-induced hopping. a,b) STM images (3.7 nm × 3.0 nm) of a propene molecule before (a) and after (b) injection of tunneling electrons ($V_S = 420$ mV, $I = 2$ nA for 4 s). The place of injection is marked with an asterisk. The molecule moves by a lattice constant along the step. Also observed as a dark figure-eight-shaped spot is a CO molecule coadsorbed on the same step edge, which serves as reference point. Exceeding the threshold of 375 meV dramatically increases the probability of this lateral translation mode.

After increasing the current to about 5 nA, we observed interconversion of the enantiomers (Figure 4 a,b). As for the rotation, the slope in the lg *R*–lg *I* plot for the hopping is 1, but 2 for the enantiomer conversion (Figure 4 c). Thus, two inelastically tunneling electrons participate in the latter process. At any bias above 375 mV all vibration modes are excited in the IET experiment, including those that couple to the translation. Hence, many rotations are observed in the current–time trace before a translation event occurs (see Figure S5 in the Supporting Information). In order to excite both steps simultaneously, an increase of the probability of excitation or the lifetime of the lateral excited state is required. On a metal surface, vibrationally excited molecular states decay quickly by energy transfer to the substrate electrons by electron–hole pair formation. With a lifetime of about only a picosecond,[19a] the probability that the vibration couples to a motion coordinate seems to be rather small. In IET, however, the number of electrons per second is in the order of 10 billion (1 nA $= 0.6 \times 10^{10}$ e s^{-1}), and even processes involving two electrons become possible at increased current. Two-electron processes have been identified, for example, for IET-induced desorption[8] and dissociation.[9]

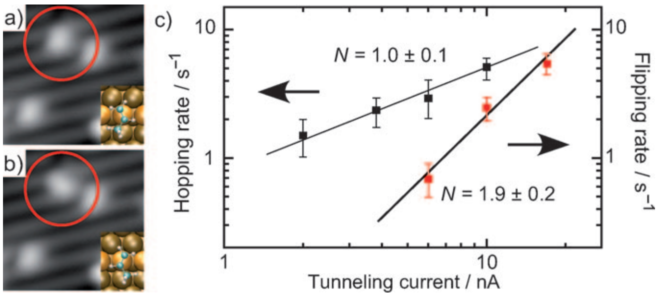

Figure 4. Interconversion of enantiomeric states of a single adsorbate molecule. a,b) STM images (4.1 nm × 4.1 nm) before (a) and after (b) injection of tunneling electrons at a bias voltage of 500 mV and $I = 5$ nA into a propene molecule (red circle). c) The reaction order for hopping at constant bias voltage $V = 420$ mV is 1, and that for enantiomer conversion is 2.

For the mechanism of the chirality conversion process the following scenarios can be considered. In principle, the molecule might be rearranged 1) by flipping over under the STM tip, 2) by inversion at the middle CH group, or 3) by isomerization through intramolecular H-atom transfer. Intramolecular proton transfer is quite common in the gas phase after resonant electron attachment.[21] However, we must point out that the lifetimes for charged species at a metal surface are much smaller (in the range of femtoseconds) than those of excited vibrations.[22]

If we assume that vibrations with sufficient lifetimes are involved in the enantiomer conversion, we may focus on those vibrations that lead to rotation and translation. In Figure 5 we schematically show energy-transfer mechanisms of all three actions observed here. For the rotation, we use the CH_3 stretching vibration as an example. At the threshold bias voltage, the molecule is in the first excited state and couples to the rotation motion (Figure 5 a). The same scenario applies for the C–H stretching–translation coupling, whereby the energy barrier coincides with the diffusion barrier along that coordinate (Figure 5 b). The scenario of the two-electron process in Figure 5 c now combines these modes. For the enantiomer conversion, however, we know that excitation of the C(sp^2)–H stretching mode is required; the second electron loss process may involve a vibration other than one of the CH_3 stretching modes. Besides the C=C stretching, this could be a highly excited low-frequency bending mode, causing the molecular backbone to wag at high rate. Such vibrational heating has been identified in particular for IET-induced dissociation.[9b]

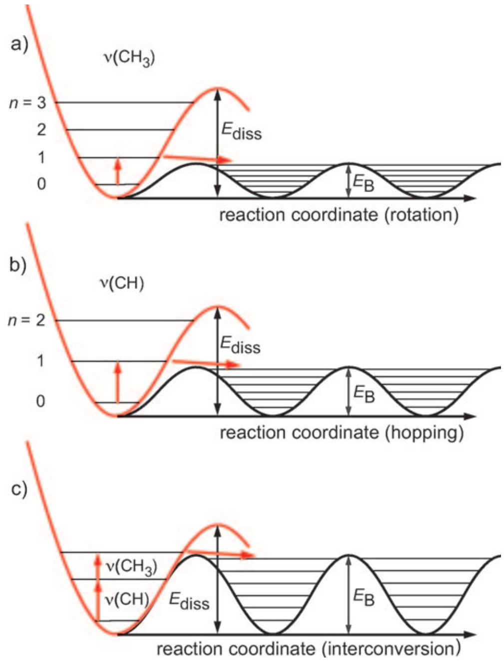

Figure 5. Principle of the mode coupling between molecular vibrations and the observed motions of a) rotation, b) hopping, and c) chirality conversion. For the latter two-electron process, a combination of the two other steps is postulated.

In the hydrogen-transfer scenario, the H atom must move from the methyl group to the methylene group; it is either kept bonded always to the molecule or to a substrate site in between. Then the molecule rotates into the opposite configuration. An intramolecular 1,2-exchange of H and Cl was postulated for the IET-induced isomerization in dichlorobenzene on Ag(111) and Cu(111) and for chloronitrobenzene on Cu(111).[23] The mechanism was proposed to include C–C stretching or C–Cl and C–H bending modes. In our case, however, no heavy Cl atoms are involved, and charge redistribution during the stretching vibrations of C and H atoms with identical electronegativity is expected to be much smaller. If we consider that the molecule is already excited by the C(sp^2)–H stretching above the diffusion barrier, i.e., the binding to the surface is decreased, the molecular inversion in the plane seems possible. This implies that the middle C–H group rotates such that the H atom moves—presumably over the center C atom—from one side to the other. A flipping of the complete molecule cannot be excluded, but in that case the molecule must remain fixed somehow between the STM tip and the surface, because desorption is expected otherwise.

For ammonia on Cu(100), the interplay of the N–H stretch and the inversion mode has been discussed in great detail in the context of the observed lateral translation (one-electron process) and desorption (two-electron process).[24] For the desorption step, two scenarios have been considered, either the ammonia umbrella mode or the doubly-excited stretching mode. For these modes, the lifetimes of the excited states have been estimated; however, the conclusions remained tentative owing to the complexity of the matter. In our case the system is even more complex, because more than twice the number of atoms are involved! At this point, we therefore cannot favor one of the above-discussed processes over the other. Simple pictures using the trajectories of atomic motion will continue to have shortcomings until meaningful theoretical efforts can describe these complex vibration-induced processes.

We have shown here that inelastic electron tunneling can invert the enantiomeric state of an adsorbate, and molecular vibrations have been identified that induce certain adsorbate motions.

Experimental Section

Methods: The copper single-crystal surface was cleaned in vacuo using standard preparation techniques as described in detail previously.[25] All STM images presented here were recorded in constant-current mode with a sample bias of 70 mV and a tunneling current of 0.3 nA. The Cu(211) crystal temperature was 7 K during imaging and 40 K when it was dosed with propene gas. We induced molecular motion by applying a voltage pulse to the sample while the tunneling current was recorded. The STM tip was positioned over the center of a molecule, the feedback was turned off, and the tip was moved vertically to give the desired initial current during the pulse. Density functional theory (DFT) simulations were performed with the plane wave pseudo-potential based code q-Espresso (P. Giannozzi et al., http://www.quantum-espresso.org; see the Supporting Information for more details).

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