

Molecular Seesaw: A Three-Way Motion and Motion-Induced Surface Modification

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Abstract: We introduce a three-way molecular motion which can be a suitable switching system in future molecule-based nanocircuits. A real-space investigation revealed that vinylferrocene adsorbs site-specifically on the Ge(100) surface and then shows a reversible tilting motion, similar to a seesaw. Unlike conventional molecular motions, it not only has three stable switching states at room temperature but also shows a motion-induced surface-structure modification, allowing surface-mediated signal transmission. Demonstrated STM-tip influence on the motion allows the feasibility of tip-induced manipulation.

To realize the “molecule-based nanocircuit”, finding the suitable system applicable to molecular switches is essential.¹ Real-space observations of reversible motions between at least two distinct stable switching states not only enable us to obtain a detailed picture of the motion but also provide insights into the switch design.² Using STM, several kinds of atomic or molecular switching systems have been demonstrated so far by site-to-site displacements,^{3,4} orientation changes of a rotating molecule,^{5,6} or conformational changes.^{7–10} However, from some points of view, a journey to find a practical switching system is just beginning. First, most of the studies on the atomic or molecular motion have been carried out at low temperatures of less than ~ 80 K since they are vulnerable to thermal noise. In order to be employed in the molecular devices operating at room temperature, finding a switch with room-temperature stability is a standing challenge. Second, studies on the molecular switch have mainly been focused on the motion of the molecule itself. To be utilized as a functional switch, an additional activity of the motion deserves to be dealt with as well.

Here, we introduce a switching system that goes beyond the bounds of conventional molecular switches. A real-space investigation revealed that a vinylferrocene molecule adsorbs on Ge(100) at a specific binding site. It not only has three stable switching states at room temperature but shows an interesting single molecular motion and the motion-induced secondary structural change in surface atoms.

Figure 1A shows a filled-state STM image taken after the adsorption of 0.02 ML of vinylferrocene onto a clean Ge(100) surface. Three dumbbell-shaped fuzzy features (dotted circles), consisting of two coupled bright protrusions on one side of a dimer, are attributed to adsorbed vinylferrocene molecules. As indicated in an enlarged STM image of this feature (Figure 1B), the measured distance between the top positions of a coupled protrusion is 3.6 Å. It agrees well with both experimental and theoretical values of 3.3 Å for the distance between the cyclopentadiene (Cp) rings in a ferrocene molecule.¹¹ Therefore, it is plausible that the bright dumbbell-shaped protrusion is associated with coupled Cp rings of a ferrocene moiety and that the molecular axis of the adsorbate is parallel to the surface.

Careful investigations based on high-resolution STM images of *parallel* vinylferrocene (*p*-VF) revealed a detailed picture of the adsorption structure. The center of the dumbbell-shaped protrusion,

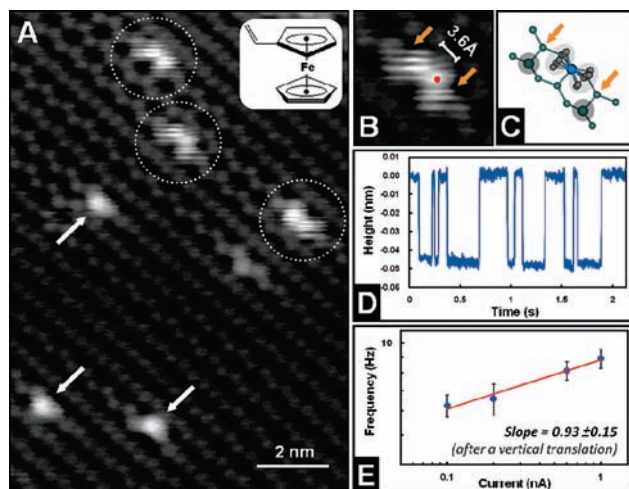


Figure 1. (A) A filled-state STM image of a vinylferrocene adsorbed Ge(100) surface acquired at room temperature ($V_S = -1.1$ V, $I_T = 0.1$ nA). The dotted circles and arrows indicate *parallel* (*p*-VF) and *tilted* (*t*-VF), respectively. (B,C) An enlarged image and a proposed schematic representation of the adsorption structure of *p*-VF. Orange arrows indicate the position of down-Ge atoms. (D) Z-t measurement for *p*-VF (A red dot in (B) is the tip position used for data collection). (E) A double-logarithmic plot of the flipping frequency of *p*-VF versus the tunnel current. After subtracting the thermal effect by the vertical translation of the data points, a slope close to unity is obtained. The error bars depict the 95% confidence interval.

the possible position of an iron atom, is exactly located on the top of an up-Ge atom (Figure 1B and 1C). As evidenced by diverse observations, we are convinced that this site-specificity indicates the presence of a chemical bond (see the Supporting Information). Since the formal charge of an iron atom in a vinylferrocene molecule is considered to be positive,¹² it is expected that a partially negative up-Ge atom will donate electrons to an iron atom, thus resulting in a Ge–Fe dative bond.

As indicated by orange arrows in Figure 1B and 1C, only a down-Ge atom has been found directly next to the Cp rings. We expect that there is an interaction between the electron-rich Cp rings¹³ and the electron-deficient down-Ge atoms at both ends of the adsorbate. Compatibly, only asymmetric dimers have been observed at the dimer row in which the *p*-VF feature is located.

Meanwhile, the local noise around *p*-VF features implies that the adsorbates are rattling. To understand the motion of the *p*-VF state, an STM tip was positioned at the center of one of Cp rings, and the apparent tip height was measured under constant current conditions. It is demonstrated that the *p*-VF geometry undergoes a flip-flop motion between two distinct states (Figure 1D). The flipping frequency shows a linear dependence on tunnel current, and an extrapolation of the relation does not intersect the origin of the graph, indicating the presence of a thermal process as well as an STM-tip effect on the motion (Figure 1E). After subtracting the

thermal effect by the vertical translation of the data points, a slope close to unity was obtained. Therefore, the STM-tip effect can be described as a one-electron process.¹⁴

Besides the rattling motion of the *p*-VF, the adsorbate undergoes a more dramatic tilting motion. We have found that the other adsorption features, arrowed in Figure 1A, are one of the switching states of the motion.

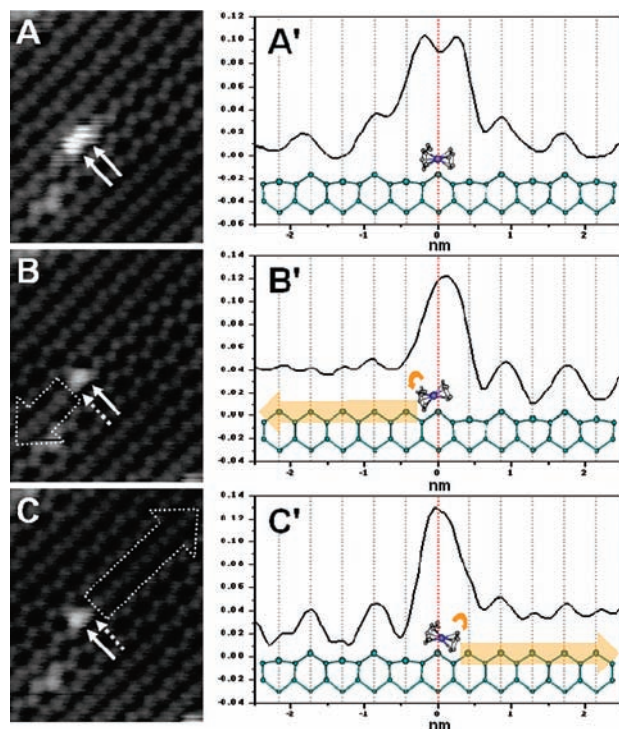


Figure 2. (A to C) A series of STM images ($V_s = -1.1$ V, $I_T = 0.1$ nA) obtained at the same scanning area describes the seesaw motion. The dumbbell-shaped *p*-VF in (A) is transformed into a new shape consisting of a bright spot (arrowed) and a less bright one (dashed-arrowed) in (B), showing that the adsorbate is no longer *parallel* to the surface but *tilted*. The position of the bright spot and the less bright spot is switched in (C), indicating another orientation of *t*-VF. In (B) and (C), symmetric dimers, enclosed by a dotted arrow, are induced exclusively at the side of less bright spot. (A' to C') Schematic illustrations with cross section line profiles of each feature.

In Figure 2, a series of STM images of the same region show the feature transformation of the vinylferrocene adsorbate. As we proceed from Figure 2A to Figure 2B, the dumbbell-shaped fuzzy feature (attributed to *p*-VF) adopts a new shape consisting of a bright spot (arrowed) and a less bright one (dashed-arrowed). The significant difference in brightness between the two protrusions in Figure 2B indicates that the molecular axis of the adsorbate is now no longer *parallel* to the surface but *tilted*. The feature in Figure 2C is also considered to be the *tilted* vinylferrocene (*t*-VF), but tilted in the opposite direction because a less bright spot appears at the other side of the dumbbell. These features are clearly imaged while *p*-VF appears as a fuzzy image. So, it is not regarded as one of the flipping states of *p*-VF. We believe that the internally bistable *p*-VF structure is metastable, and by any chance, it settles down one of two possible tilting states, like a seesaw. The geometry transformation from the *tilted* feature to the *parallel* structure has also been observed, which indicates the motion is reversible. As we discussed, the center of the molecule is anchored to the surface via the Ge–Fe coordinative bond, and there are additional interactions at both ends of the adsorbate. We expect that this unique adsorption structure causes the molecule to show the seesaw-like behavior.

More interestingly, it is also observed that the seesaw motion triggers a long-range modification of the surface structure. Schematic representations with the corresponding cross section line profiles are shown in Figure 2A' to 2C'. In the case of *p*-VF (Figure 2A), as we mentioned, the nearest Ge–Ge dimer is frozen in the buckled configuration, and thus the asymmetric dimers are induced at both sides of the *p*-VF structure. On the other hand, in the *t*-VF feature (Figure 2B and 2C), the strongly induced dimer buckling in *p*-VF is now changed to a symmetric configuration at one side of the adsorbate, exclusively at a down-Cp side. We believe that the geometry change of the adsorbate delocalizes the electron distribution of the neighboring Ge dimer at the down-Cp side, and it finally initiates a successive dimer reconstruction along the dimer row—similar to dominoes falling. Once *t*-VF is converted into *p*-VF, the asymmetric dimers are produced again at both ends.

This motion-induced unidirectional surface modification is continued along the specific dimer row unless it faces a defect on the dimer, normally continued to several nanometers in our experiments. Thus, in future molecule-based devices, it is able to transfer the energy to the other node in a circuit and trigger the secondary effect without any additional interconnecting materials.

We have also observed STM-tip effects on the seesaw motion. The ratio of feature population was changed by modulating the sample bias voltage. A series of STM images revealed that the portion of the *p*-VF feature dramatically increases (36% \rightarrow 61%) as the sample bias increases (-1.1 V \rightarrow -2.0 V), implying the extended lifetime of the *p*-VF at higher voltage conditions (see the Supporting Information). Furthermore, in the tip height measurements, where the STM-tip position is fixed over the molecule, the feature transition between *p*-VF and *t*-VF states has not been recorded for the total data acquisition time of 455.4 s (see the Supporting Information). It is conceivable that the fixed STM-tip position directly over the molecule pinned the adsorption state into the *p*-VF state. The STM-tip influence on the motion allows the feasibility of tip-induced manipulation at room temperature. We believe the manipulation of the seesaw motion deserves further experimental attention.

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Supporting Information Available: Experimental details, evidence of chemisorption, a series of STM images, and sample bias dependence of feature lifetime showing STM-tip effects on seesaw motion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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