

Propagation of Conformation in the Surface-Aligned Dissociation of Single CH_3SSCH_3 Molecules on Au(111)

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Studies of single-molecule reactions on surfaces using scanning tunneling microscopy (STM) provide unprecedented insight into the structure of reactants and products, as well as the reaction pathways.^{1–4} Several previous STM studies detailed the trajectories of atomic fragments produced by electron dissociation of adsorbed molecules.^{5–7} In particular, it was found that if the dissociating bond is aligned with the adsorption sites of the products the latter are quickly trapped and the bond geometry of the reactant molecule can be “imprinted” on the surface.⁶ However, since the majority of the studied reactions involved the ejection of atomic species, no information about the conformation of the products was accessible.

We have studied the dissociation of the CH_3SSCH_3 molecule adsorbed on the Au(111) surface using STM. CH_3SSCH_3 is dissociated by the tunneling current to produce two CH_3S species.⁸ Since CH_3S is a polyatomic species, it is possible to track the conformational changes involved in the reaction. We find that the ubiquitous geometrical *trans*-conformation of the CH_3 groups in the parent CH_3SSCH_3 molecule is retained with a high probability as the CH_3S species are ejected away from each other.

The experiments were conducted with a commercial low-temperature STM (Omicron Nanotechnology) using etched tungsten tips. The Au(111) crystal was cleaned by Ar^+ sputtering and annealing to 773 K. CH_3SSCH_3 was purified using several freeze–pump–thaw cycles and deposited through an effusive beam doser on the crystal at <10 K. The STM images were taken at a temperature of 5 K, tip–sample bias of 30–50 mV, and tunneling current of 50–100 pA.

Single CH_3SSCH_3 molecules (Figure 1a) are imaged as ellipses with two lobes of the same apparent height (see line scans in Figure 1b). The bright lobes originate from the CH_3 groups judging by their peripheral position in the STM image.^{8,9}

To assign *cis*- or *trans*-conformation of the adsorbed CH_3SSCH_3 molecule (Figure 1), we determined the position of Au atoms in the surface lattice using isolated CO molecules as markers.^{10,11} The symmetry of the CH_3SSCH_3 molecule combined with that of the underlying surface lattice (red circles Figure 1c) is described by an inversion center located in the geometrical center of the CH_3SSCH_3 image (black dot in Figure 1c). Such a centrally symmetric arrangement (molecule + lattice) can be produced only by the *trans*- CH_3SSCH_3 because the *cis*-isomer would not have such an inversion center but would have a symmetry plane as shown in Figure 1d. A schematic model of the *trans*- CH_3SSCH_3 molecule derived from the STM measurements is shown in Figure 1e; the S–S bond is aligned with the close-packed direction on the Au(111) surface and is located above the Au–Au bridge site. A similar structure was also proposed theoretically.¹²

Dissociation of a single CH_3SSCH_3 molecule can be accomplished by applying a low-current pulse with the surface positively biased at a voltage of ~ 1.4 V. The dissociation likely occurs via electronic excitation of the molecule due to the relatively high threshold energy. Surprisingly, the *trans*-conformation of the

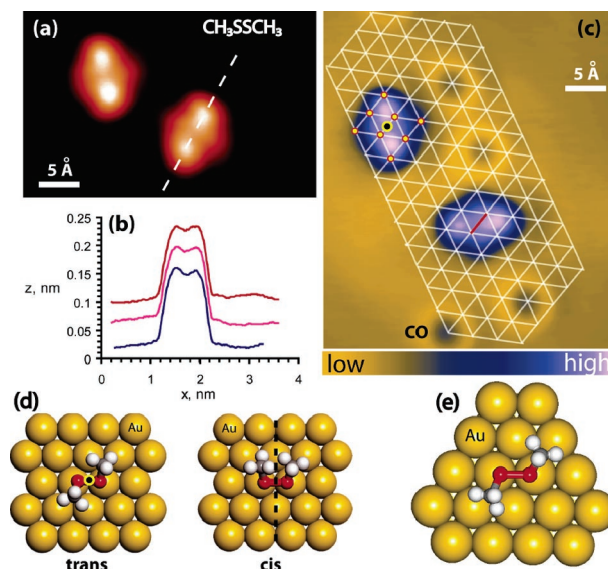


Figure 1. (a) STM image of two CH_3SSCH_3 molecules on Au(111). Both molecules are *trans*-conformers (see text). (b) Line profiles of several CH_3SSCH_3 molecules taken along the white dashed line in (a). (c) Triangulation of CH_3SSCH_3 molecules using CO molecules adsorbed on atop Au sites. The black dot in the upper molecule marks the position of the inversion center. (d) Comparison of *cis*- and *trans*-symmetry for CH_3SSCH_3 . In (c) and (e), the red line marks the direction of the S–S bond.

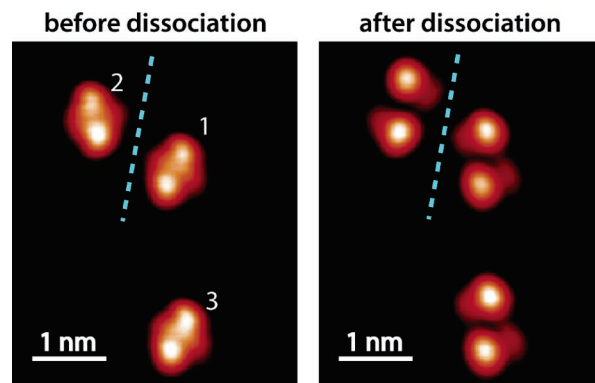


Figure 2. Electron-induced dissociation of CH_3SSCH_3 molecules on the Au(111) surface as seen by STM. The products retain the conformation and orientation of the parent molecules: CH_3SSCH_3 molecules 1 and 3 are identical, producing identical CH_3S *trans*-pairs. Molecules 1 and 2 are offset mirror images of each other, and so are the product *trans*-pairs of CH_3S species (dashed blue line is the mirror plane).

parent CH_3SSCH_3 molecule is often reflected in the relative position and alignment of two product CH_3S species, which are grouped into *trans*-pairs as seen in Figure 2. The orientation of the CH_3SSCH_3 molecule on the surface (the direction of its S–S bond) is also retained in dissociation because the *trans*-pairs are related

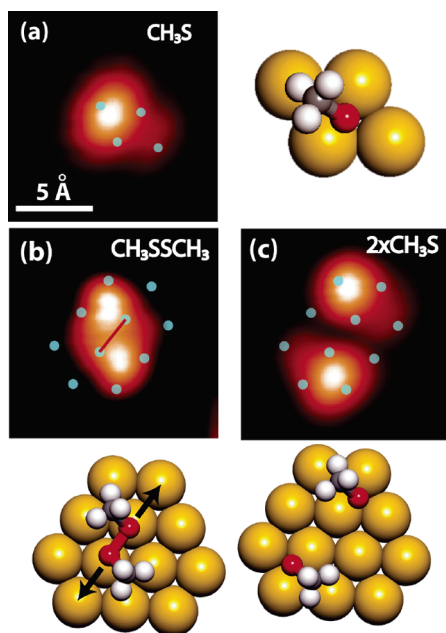


Figure 3. (a) STM image and structural model of isolated CH_3S species adsorbed on the Au–Au bridge site.⁸ Blue dots mark Au atoms in the lattice. (b) Undissociated CH_3SSCH_3 molecule (red line is the direction of the S–S bond). (c) The *trans*-pair of CH_3S species produced by electron-induced dissociation of (b). The models show the schematic of the surface-aligned dissociation of CH_3SSCH_3 .

to each other by the same symmetry operations as their parent CH_3SSCH_3 molecules (Figure 2).

In our detailed study of CH_3S on the Au(111) surface,⁸ we established that the CH_3S species adsorbs with the S-headgroup on the bridge Au–Au site (with a slight shift toward the hollow site) as shown in Figure 3a. Comparison of Figure 3a and 3c allows one to determine the adsorption configuration of the *trans*-pair: the CH_3S species are separated along the parent direction of the S–S bond by two lattice spacings (5.5 \AA), and the S–C bond directions in the CH_3S species match closely those of the parent CH_3SSCH_3 molecule. Thus, CH_3SSCH_3 dissociation is simultaneously bond-aligned because the products are ejected along the S–S bond direction and surface-aligned because the products are trapped on the surface sites aligned with the breaking bond. This is similar to the *localized atomic reaction* of chlorinated benzene molecules on the Si(111) surface.¹³

To estimate the likelihood of the conformation retention in the dissociation of the CH_3SSCH_3 molecule, we chose the pulsing condition so that the yield of the reaction is high, but the tunneling current and the magnitude of the electric field during the pulse are low. This was achieved at $U = +1.4 \text{ V}$, $I = 20 \text{ pA}$, and pulse duration = 100 ms.

Out of 485 dissociation events, 358 produced the *trans*-pairs of CH_3S species with the same conformation as the parent CH_3SSCH_3 molecules. The probability of such a scenario is therefore $74 \pm 4\%$. This conformational retention is dramatic when considering the large number of possible alternate dissociation scenarios involving in-plane and out-of-plane rotation of the S–C bonds,

which will disrupt the conformational coherence between the CH_3SSCH_3 molecule and its dissociation products.

The major such alternate scenario (25% of all the events) involved hopping of the CH_3S species between several neighbor bridge sites after the S–S bond is broken. Each multisite hop is followed by a 60° in-plane rotation of the S–C bond. The fairly low probability of this pathway arises from strong binding of the CH_3S species on the Au(111) surface,¹⁴ which quickly get trapped by the surface after dissociation.

Out-of-plane rotation of CH_3 groups around the S–S bond can occur in the transition state of the dissociating CH_3SSCH_3 molecule. A very small number of dissociation events (<2%) followed this pathway with the out-of-plane rotation of one of the two CH_3 groups. The CH_3S pair in this case is imaged in a *cis*-configuration. No events involving out-of-plane rotation of both CH_3 groups were observed.

The lack of out-of-plane rotation of CH_3 groups is unexpected because bond dissociation is accompanied by substantial vibrational and rotational heating of the product species. This can be explained using a well-known principle in transition state theory⁶ that new bonds are created while the original ones are broken. In the case of the CH_3SSCH_3 molecule, the surface-alignment of the dissociation process allows the formation of the bridge-bonded CH_3S species to be synchronized with the elongation of the S–S bond. The rotation of the CH_3 group in the transition state will then likely be hindered because of high coordination of the S-headgroup to surface Au atoms along the reaction pathway.

In summary, we have determined that, in the case of electron-induced CH_3SSCH_3 dissociation on the Au(111) surface, the arrangement of the product CH_3S species on the surface preferentially retains the conformation and orientation of the parent molecule.

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