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# Observation of *cis*-2-butene molecule on Pd(1 1 0) by cryogenic STM: site determination using tunneling-current-induced rotation

Y. Sainoo [a,b], Y. Kim [b], T. Komeda [b,*], Maki Kawai [b], H. Shigekawa [a]

[a] *Institute of Applied Physics, CREST, University of Tsukuba, Tsukuba 305-8573, Japan*
[b] *RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

## Abstract

We have investigated the bonding configuration of an isolated *cis*-2-butene molecule ($CH_3$–$CH$=$CH$–$CH_3$) on the Pd(1 1 0) surface using a cryogenic STM at the sample temperature of 4.7 K. For the precise determination of the bonding site of the molecule, we utilize a novel method of rotating the molecule by injecting tunneling electrons into the molecule. We have observed the rotation of the molecule around the terminal site of a single Pd atom with hopping between four equivalent bonding sites when tunneling electrons with the energy of 170 meV were dosed. The bonding between the *cis*-2-molecule and the Pd(1 1 0) surface is considerably through π-bonding at the carbon double-bond, which makes bonding on the terminal site favorable. However, the analysis of the images of rotating molecule reveals that the $C$=$C$ is shifted from the terminal site and located at the off-symmetry position.
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The determination of bonding configuration of hydrocarbon molecules has attracted attentions for a long time which is partially due to the fact that the adsorption site and the orientation of adsorbates play a key role in the catalytic reaction, such as hydrogenation reaction of hydrocarbons [1,2]. In addition, recent rising interest for the hybridization between bio-molecules and semi-conductor or metal surface should demand more information of the bonding configuration of large molecules.

It has been demonstrated scanning tunneling microscopy (STM) has a high capability in observing adsorbed molecules in a real space. Furthermore, STM can manipulate individual atoms and molecules. Especially recent studies have demonstrated that the vibrational excitation of

* Corresponding author. Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan. Tel.: +81-22-217-5368; fax: +81-22-217-5404.
*E-mail address:* komeda@tagen.tohoku.ac.jp (T. Komeda).

adsorbates caused by tunneling electrons can be the energy source in producing certain selective dynamic motions and reactions [3–6].

In this paper, we study the bonding configuration of *cis*-2-butene molecule ($CH_3$–$CH$=$CH$–$CH_3$) on Pd(1 1 0) at 4.7 K with a novel method of rotating the molecule by the injection of tunneling electrons. We successfully rotate the *cis*-2-butene molecule around a single Pd terminal site, and four stable bonding configurations are identified around the single Pd terminal site. The images are well explained if we assume a model where the *cis*-2-butene molecule adsorb on a single Pd atom with a π-bond manner, though the center of the carbon double-bond is shifted from the terminal site of a Pd atom.

A clean Pd(1 1 0) surface was prepared by the standard cleaning technique with a repetitive $Ar^+$ sputtering and annealing cycles. The molecules (99% purity) were dosed through a dosing tube located close to the sample surface at the substrate temperature below 50 K. A mechanically sharpened and field-emitted tungsten wire was used as the STM tip. All STM measurements were performed at 4.7 K.

Fig. 1 shows the STM image of the Pd(1 1 0) surface where isolated *cis*-2-butene molecules are adsorbed. On the same surface, *trans*-2-butene molecules are dosed in addition as reference molecules. The Pd rows are in the direction from upper-left to lower right. The images of *cis*-2-butene molecules appear as oval protrusions. Furthermore the oval is asymmetric and has bright region (head) and dark region (tail) as an internal structure. Thus there exists a single symmetry line in the image of the *cis*-2-butene molecule, which is along the long axis of the oval.

With the angle of the image of Fig. 1 where Pd rows are in the diagonal direction, STM images of *cis*-2-butene molecules appear elongated either vertically or horizontally; i.e., the symmetry line of the molecules is either vertical or horizontal. In addition, the head is located either in the upper side or in the lower side of the molecule in vertical molecules (right or left side for the horizontal molecules). Thus we can identify totally four types of images for isolated *cis*-2-butene molecules which are marked in Fig. 1 as $C_U$, $C_D$,


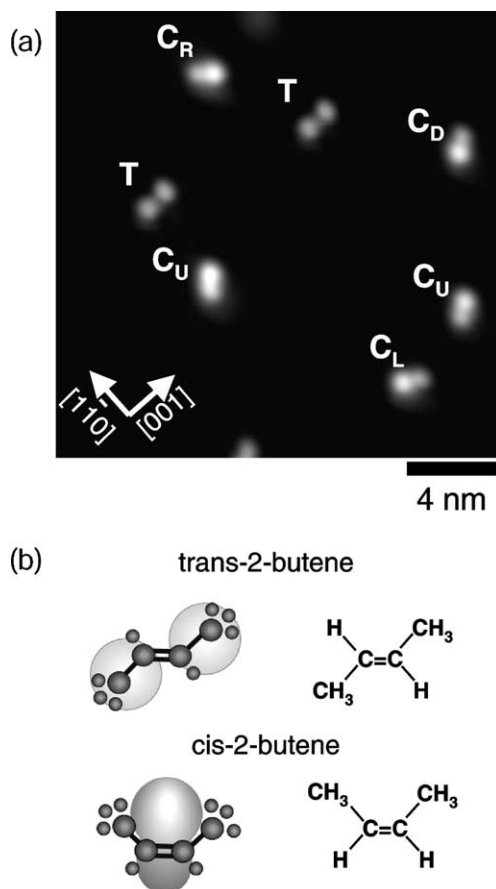
Fig. 1. (a) An STM image of *cis*-2-butene molecules adsorbed on the Pd(1 1 0) observed at 4.7 K. The marks $C_R$, $C_L$, $C_U$, and $C_D$ correspond to different bonding configurations (see text). Molecules of *trans*-2-butene are also dosed for comparison, which are marked by T. Imaging conditions are $V_{sample} = -20$ mV and $I_{tunnel} = 1.0$ nA. (b) Schematic models for the molecules of *trans*-2-butene and *cis*-2-butene, where the circles with grid-pattern correspond to the bright area in the STM images.

$C_R$, $C_L$ where the suffix corresponds to the relative location of the head; up, down, right and left, respectively. Since the substrate Pd(1 1 0) has the $C_{2v}$ symmetry, the existence of four types of STM images corresponds to a single bonding configuration of *cis*-2-butene with off-symmetric manner.

As is marked by T in Fig. 1, the STM image of the *trans*-2-butene molecule, which is an isomer of *cis*-2-butene, appears as a paired protrusion. We have analyzed the bonding configuration of *trans*-

2-butene molecule on Pd(1 1 0) in previous papers [6,7], and concluded that the bright spots correspond to the positions of $CH_3$. This is considerably derived from the bent configuration of the C=C–C, in addition to the distribution of the electron's density of state at the position of $CH_3$ in the highest occupied molecular orbital (HOMO) of a *trans*-2-butene molecule. In analogy we consider that the head of the *cis*-2-butene molecule corresponds to the area marked by a large shaded circle in Fig. 1(b), to which side both $CH_3$ species are located. Consequently the symmetry line of the image of the *cis*-2-butene molecule is perpendicular to the carbon double bond.

Here we try to identify the bonding site of the *cis*-2-butene molecule by inducing the rotation of the molecule with the injection of the tunneling electrons into a molecule. It has been demonstrated that the dosing of tunneling electrons on an adsorbed molecule can cause surface phenomena such as hopping [5], rotation [3], and chemical reaction [4,6]. The dosing of tunneling electrons in the present experiment was carried out by positioning the STM tip above the top of the head of the molecule followed by turning-off the feedback-loop and changing the bias voltage from the one for the observation.

The rotation of the molecule manifests itself in the variation of the tunneling current, which is shown in Fig. 2(a). Similar results have been reported for the rotation of the $C_2H_2$ molecule on Cu(1 0 0) [3,8]. Fig. 2(a) corresponds to the case where the energy of the tunneling electrons is 60 meV, and the tunneling electrons are dosed in the isolated molecule of $C_R$ in Fig. 2(b). The tunneling current shuttles the high state ($I_1$) and the low state ($I_2$). The current is in the high state at the beginning of the electron injection, and is in the low state at the end of the dosing. The corresponding STM image of the molecule is observed as $C_R$ at the initial state and as $C_D$ at the final state, which suggests that high state corresponds to $C_R$ and low state corresponds to $C_D$ when the tip is positioned at the marked position in the figure.

By repeating the dosing of tunneling electrons to the $C_R$ molecule and the observation of the molecule's azimuth rotation, we have found that, with the bias voltage of 60 mV, the $C_R$ molecule
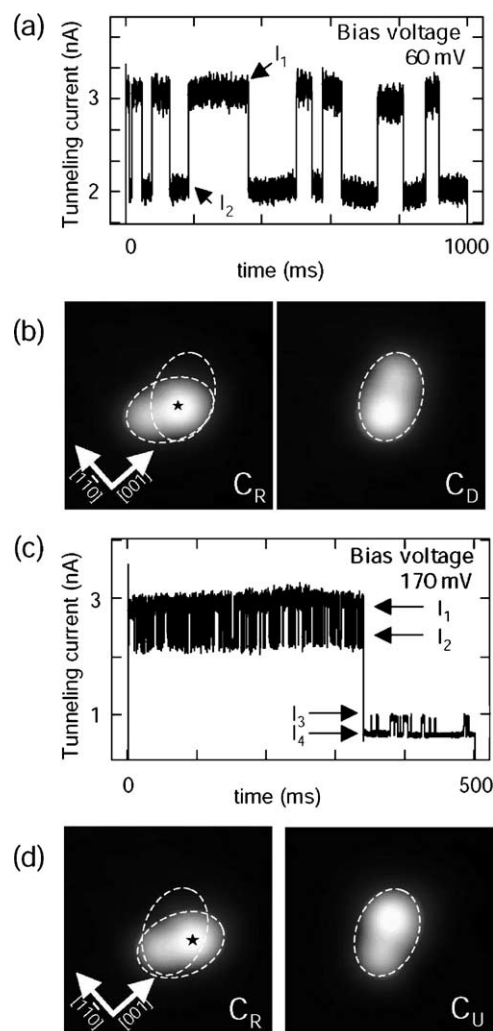


Fig. 2. (a) The variation of the tunneling current when the tunneling electrons with the energy of 60 mV are injected on an isolated *cis*-2-butene molecule. The configuration of the molecule corresponding to this current change is shown in (b); we started the dosing of the tunneling electrons on the molecule of the $C_R$ configuration at the position marked by a star, which ended with the $C_D$ configuration. (c) The variation of the tunneling current when the bias voltage was 170 mV. The change of the molecule's configuration is shown in (d); the dosing was started with the $C_R$ configuration and ended at the $C_U$ configuration.

rotates only to $C_D$. The rotation of $C_R$ molecule to $C_L$ or $C_U$ state occurs when the energy of the tunneling electrons is 170 meV. The current variation for this case is shown in Fig. 2(c).

The tunneling current has four stable current states; $I_1$, $I_2$, $I_3$ and $I_4$ in Fig. 2(c). The states of $I_1$ and $I_2$ are identical with the ones in Fig. 2(a). A big drop of the current can be seen at $\sim$330 ms. The current shuttles the state of $I_3$ and $I_4$ after that moment. The final STM image of the molecule corresponds to $C_U$. After repeating the experiments, we conclude that the $I_3$ corresponds to $C_L$ and $I_4$ to $C_U$.

The rotation of the *cis*-2-molecule with the dosing of the tunneling current can be simplified if we assume the pairs of ($C_R$, $C_D$) and ($C_L$, $C_U$). The intra-pair rotation can be induced by dosing tunneling electrons with the energy of 60 meV, but the inter-pair rotation is only observed with a higher bias voltage of 170 meV. We speculate that the potential barrier for the inter-pair rotation is higher than that of intra-pair rotation.

With the control of the bias voltage and monitoring of the tunneling current, the *cis*-2-butene molecule can be rotated to one of the four stable bonding configurations. Now we make the registration of the *cis*-2-butene molecules on the Pd(1 1 0) surface using this technique.

Fig. 3(a)–(d) show the high-resolution images of a single *cis*-2-butene molecule at the four stable configurations obtained by rotating a single molecule. The lattice grid of the substrate is obtained by imaging the same surface with a molecule on the apex of the STM tip. It has been reported that high-resolution images can be obtained with this method [9]. In addition to the lattice grid, the symmetry lines of the molecules at the four stable positions are superimposed.

It is interesting to notice that the four images of the *cis*-2-butene molecules rotate around the terminal site of a single Pd atom. In addition, four symmetry lines form rhombus instead of intersecting at the terminal site or at the short-bridging site. In previous works, we have studied the bonding configurations of ethylene and *trans*-2-butene molecules on the Pd(1 1 0) surface [6,7,10,11]. In both cases, the molecules show π-bond character and occupy the terminal site. Considering the existence of C=C in the *cis*-2-butene molecule similar to the cases of the ethylene and the *trans*-2-butene molecules, we are tempted to assume a similar bonding configuration for the
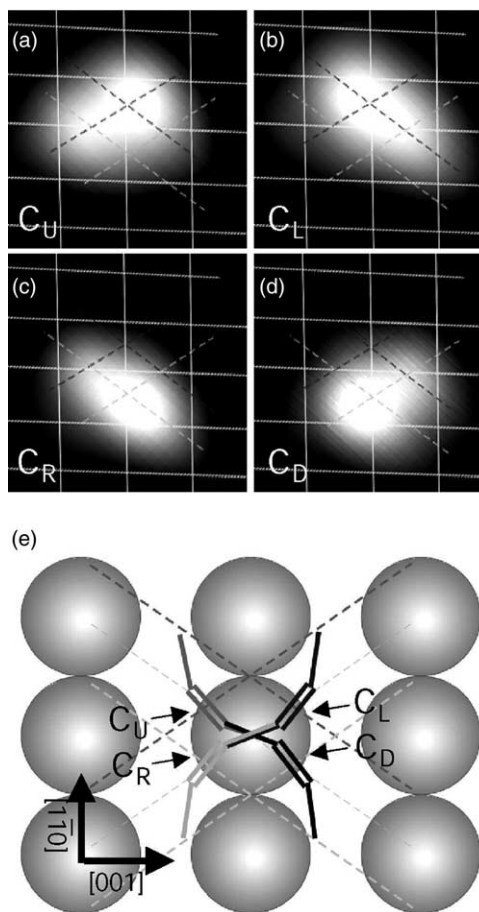


Fig. 3. (a)–(d) The STM images of the *cis*-2-butene molecules at the four stable configurations, which are obtained by rotating a single molecule by the injection of the tunneling electrons. The superimposed grid is the registration of the Pd(1 1 0) substrate, which is obtained with a molecule-coated tip (see text). Four lines which form a rhombus correspond to the symmetry line of the molecule at the four stable azimuth rotations. (e) Schematic models for the bonding configuration of the *cis*-2-butene molecule on Pd(1 1 0) at the four stable configurations. For each configuration, the positions of the double bond and CH$_3$ are schematically shown.

*cis*-2-butene molecule and the double bond at the terminal site. However, if the carbon double bond is located on a terminal site, the symmetry lines of the molecules at the equivalent bonding configurations should intersect at the terminal site [12].

Instead we would propose a model for the bonding configuration, which is schematically

drawn in Fig. 3(e) where the double bond and the CH$_3$ are illustrated by bars. The bonding site of the double bond is not on the terminal site of the Pd atom; instead the bonding position of the double bond is shifted from the terminal site of the Pd atom while keeping the π-bonding character between the molecule and the substrate. The reason why the *cis*-2-butene occupies such unsymmetrical position on the Pd(1 1 0) is unclear at this moment, and further theoretical calculation is necessary. However, we believe the technique of rotating molecule by the tunneling current, which is shown in this paper, can be a powerful tool to determine the bonding configurations of large molecules.

In summary we have investigated the bonding configuration of the *cis*-2-butene molecule on the Pd(1 1 0) surface with a novel method of rotating the molecule by the injection of tunneling electrons into the molecule. It is detected that the molecule rotates around the terminal site of a single Pd atom with hopping between four equivalent bonding sites, when tunneling electrons with the energy of 170 meV are dosed. It is concluded that the bonding site of carbon double bond of the *cis*-2-butene molecule is shifted from the terminal site of the Pd atoms, which shows a difference from the cases of ethylene and *trans*-2-butene molecules that also have carbon double bonds in the middle of the molecule.

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