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Electric field response of a vibrationally excited molecule in an STM junction

Michiaki Ohara,[1,2] Yousoo Kim,[1,*] and Maki Kawai[1,2,†]

[1]*Surface Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[2]*Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan*

We found that a single molecule in a vibrationally excited state on a surface can be delivered precisely to a desired position with the aid of a local electric field in a scanning tunneling microscope (STM) junction. An individual CH_3S molecule on a Cu(111) surface hops laterally to move away from a negatively charged STM tip and to come toward a positively charged tip when the lateral hopping motion is induced by inelastically tunneled electrons and the molecule is positioned in an inhomogeneous electric field. These experimental findings reveal that a vibrationally excited molecule on a surface responds with high sensitivity to a local electric field in an STM junction.

Nanoscale fabrication of well-defined molecular assemblies can provide insights into intermolecular interactions and correlation effects between neighboring molecules, and opens possibilities for novel or enhanced structural and functional properties of materials. The scanning tunneling microscope (STM) has been widely used for positioning individual molecules to fabricate molecular assemblies on surfaces. In earlier experiments, molecules were manipulated laterally by pushing, pulling, and sliding methods[1–3] and vertically by lifting methods[2,4] at surfaces. In conventional methods, the direct interaction between a molecule and an STM tip, by means of van der Waals or chemical forces, for example, has been utilized to position the molecule. The other approach for inducing the lateral motion of a molecule on a surface is to utilize vibrational excitation by means of inelastic tunneling. Komeda *et al.*[5] reported lateral hopping motion of an individual CO molecule on Pd(110) surface induced by multiple excitations of the vibrational mode along the reaction coordinate (RC) using inelastically tunneled electrons. However, because vibrationally enhanced molecular motion usually has been governed by its stochastic nature, no one has yet succeeded in precisely controlling a molecule's hopping direction and distance.

To achieve precise control of molecular position through vibrational excitation, it is necessary simultaneously to select the hopping direction and to place the vibrational excitation in the mode corresponding to the RC for hopping. To satisfy these requirements, we focused on *a local electric field in an STM junction*. In an STM junction, a local electric field is automatically generated when a bias is applied. Moreover, the magnitude of the electric field can be changed gradually, depending on the bias voltage applied to an STM tip. Surprisingly, however, the effect of a local electric field in an STM junction on the lateral hopping motion of a single molecule on the surface has not been investigated previously. Fundamental understanding of the electric field response or effect of lateral molecular hopping in the junction could be also essential to the development of molecular architectures with switch functions. Furthermore, it is desirable to control the nature of this response at the single molecule level.

In our experiments, we injected or extracted tunneling electrons at an off-center position of a single methylthiolate (CH_3S) molecule on Cu(111) to reveal the relationship between STM tip position and the direction and distance of the lateral hopping motion of the target molecule. We found that the molecule can be positioned precisely at a desired position on the surface by means of the electric field. The controllability of the manipulation drops as the electric field gradient levels off. These experimental findings clearly reveal that an inhomogeneous electric field in an STM junction greatly determines the lateral hopping direction and the distance of a vibrationally excited molecule on the surface, although the local electric field itself is a small perturbation. We propose in addition that this electric field response can be a novel method for molecular positioning when combined with vibrational excitation.

All STM measurements were carried out with a low-temperature STM.[6] The CH_3S molecules on Cu(111) appear as ball-shaped protrusions in the STM image and occupy both fcc and hcp hollow sites with equal probability.[7] The molecule can hop randomly between the two types of hollow sites [Figs. 1(a)–1(c)] when the tunneling electrons are injected into the molecular center from the STM tip.[7,8] To show the random hopping phenomenon of a CH_3S molecule, we induced a total of 60 hopping events and the probability to occupy the final adsorption sites that the molecule resides after the hopping [Figs. 1(d) and 1(e)]. The probability for all three nearest-neighbor hollow sites were equal of 0.33. The mechanism of this lateral hopping motion has been explained from the dependence of the hopping probability of CH_3S on Cu(111) on the sample bias voltage [Fig. 1(f)]. As shown in the figure, two thresholds are clearly observed at bias voltages of 85 and −85 mV, respectively, which correspond to the vibrational excitation energy of the C-S stretching mode (ν_{C-S} mode) of an isolated CH_3S molecule on Cu(111).[7,8] This means that vibrational excitation of the ν_{C-S} mode is associated with the hopping motion, and that it can be excited by both injection and extraction of tunneling electrons of more than 85 meV energy. In tunneling electron extraction, as in injection, the hopping motion is completely random in direction, when STM tip is set on the molecular center.

In this Rapid Communication, we measured the power-law dependence of the hopping rate "*R*" on tunneling current
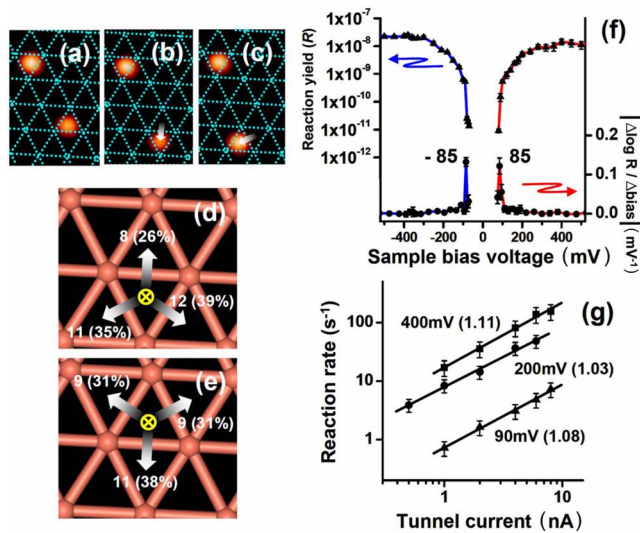
FIG. 1. (Color online) [(a)–(c)] Sequential STM images of the hopping motion of a CH_3S molecule on Cu (111). The CH_3S molecule, indicated by a yellow/light gray arrow, hops randomly by the injection of tunneling electrons into the molecular center. Random hopping was also observed when the tunneling electrons were extracted from the molecular center. [(d) and (e)] The probability of hopping events from the hollow site indicated by $\otimes$ to next-neighbor hollow sites. The $\otimes$ shows the center of the CH_3S molecule on the surface and the fixed position of an STM tip in the excitation of lateral hopping. (f) Reaction yields per incident electron for the hopping motion of the CH_3S molecule as a function of sample bias voltage for a constant tunneling current of 1 nA (upper trace:—▲—with error bar). The lower trace "—●—with error bar" represents the slopes of the reaction yield per incident electron. (g) Hopping rate R for the hopping motion of an isolated CH_3S molecule as a function of tunneling current I for various applied sample bias voltages. Solid lines are the results of least-squares fits to the data, whose slope for a given applied bias voltage corresponds to the power n in the nonlinear power-law dependence. Here, R is proportional to I^n.

"I" to estimate the hopping barrier height of a CH_3S molecule on Cu(111). Here, R is proportional to "I^n," where "n" is the order of the molecular hopping. Typical "R-I^n" plots are shown in Fig. 1(g). The slope (n) of the fitted lines in the sample bias voltage region between 90 and 400 mV is almost unity. From this power-law dependence, one can estimate that one quantum of ν_{C-S} mode is sufficient to overcome the hopping barrier. Therefore, the hopping barrier height of a CH_3S molecule can be determined to be lower than 85 meV, which corresponds to the vibrational excitation energy of the ν_{C-S} mode of the molecule.

We found that an isolated CH_3S molecule on Cu(111) repeatedly hops to the nearest-neighbor hollow site to move away from the STM tip with the injection of tunnel electrons into the off-center position of the molecule [the repulsive hopping; Fig. 2(a)–2(d)]. We further observed that the molecule hops toward the STM tip when tunneling electrons are extracted from an off-center position in the molecule [attractive hopping; Fig. 2(e)–2(h)]. The experiment was carried out as follows. After the STM image [Fig. 2(a)] was taken, the STM tip was positioned at off center of the target mol-
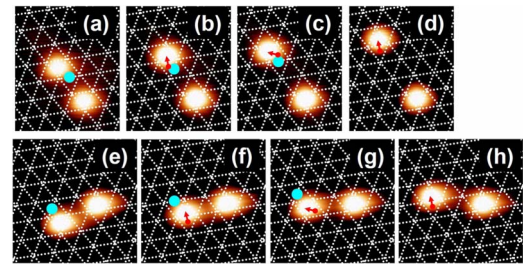

FIG. 2. (Color online) [(a)–(d)] Sequential STM images showing the repulsive hopping of an isolated CH_3S molecule on Cu(111). A tunneling current of 6.7 nA with a sample bias voltage of 400 mV was typically applied to the target molecule for 100 ms. [(e)–(h)] Sequential STM images showing the attractive hopping of an isolated CH_3S molecule on Cu(111). A tunneling current of 8 nA with a sample bias voltage of −200 mV was typically applied to the target molecule for 5 ms. The STM tip was fixed at the specified position in the molecule during the electron injection or extraction. Each blue/dark gray-filled circle indicates the electron injection (or extraction) point; each red/gray arrow indicates the lateral hopping direction on the surface.

ecule. The feedback loop was then turned off and the tunneling electrons with the preset tunneling current were injected into or extracted from the molecule to induce the molecular hopping. The position of the STM tip is shown by a blue dot in each image. After the hopping, the same surface area was rescanned to confirm the hopping direction and the distance, e.g., Fig. 2(b). Based on this evidence, we propose a model for controlling the molecule's hopping direction and distance. The tip position relative to the hopping direction of the molecule during injection (or extraction) of tunnel electrons is summarized in Fig. 3(a)–3(c).

To explain the mechanism of the controlled molecular hopping, we focused on the relationship between the charge on the STM tip determined by the applied bias voltage and
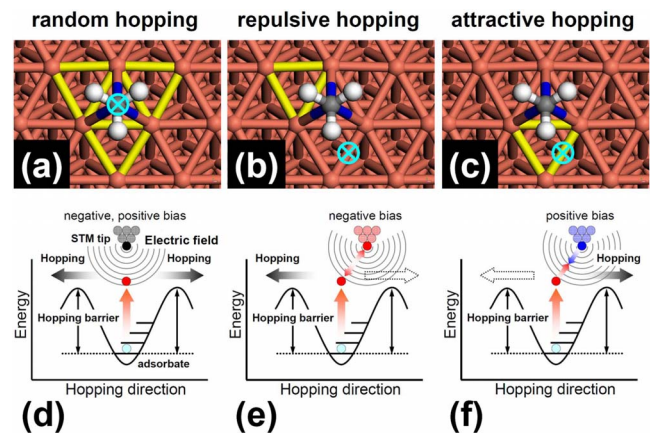

FIG. 3. (Color online) Top views of the relative position between the hopping direction(s) and the STM tip in (a) random, (b) repulsive, and (c) attractive hopping motions. The molecule hops toward the hollow sites, marked by yellow lines, when the tunneling electrons are injected (or extracted) at the positions indicated by $\otimes$. Schematics for (d) random, (e) repulsive, and (f) attractive hopping. Each electric field contour is depicted with a point charge at the STM tip apex.
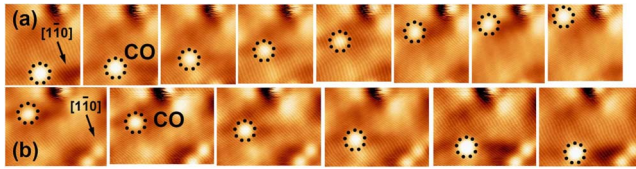
FIG. 4. (Color online) Sequential STM images showing (a) the repulsive hopping and (b) the attractive hopping of an isolated CO molecule on Pd(110), by locating the STM tip at the off center of the molecule. A CO molecule on Pd(110) appears as a ball-shaped protrusion in the STM image. It has been reported that a CO molecule on Pd(110) can hop laterally along the metal row of the surface as a result of vibrational excitation (Ref. 7). In repulsive hopping, $V_{sample}=600$ mV and $I_{tunnel}=24$ nA were typically applied to the molecule for 50 ms. In attractive hopping, $V_{sample}=-600$ mV and $I_{tunnel}=24$ nA were typically applied for 50 ms.

the hopping direction of the molecule. The STM tip was negatively charged during the injection of tunnel electrons into the molecule and positively charged during extraction. We estimated the tip-substrate distance both from an assumption that the "gap resistance" is 0.1 GΩ, when "d(=gap distance)" is 8 Å,[9] and from the fact that with our STM d is increased by 1 Å when the tunneling current is reduced by one-tenth[10] to explain our experimental observations. Based on this semiempirical method, the tip-surface distance was assumed to be ≈0.74 and ≈0.78 nm for applied sample bias voltages of −200 (attractive hopping) and 400 mV (repulsive hopping), respectively.[11] Thus, the magnitudes of the electric fields under the apex of the tip in an STM junction can be roughly estimated to be about 270 mV/nm for attractive hopping and 513 mV/nm for repulsive hopping, respectively. This is because the electric field is intensified at the sharp apex of the tip when the bias voltage is applied there.[12] Moreover, it has been widely accepted that charge transfer from several metal substrates to alkylthiolates occurs. For example, electron transfers of 1.4 electrons in C_2H_5S on Cu(111),[13] 0.3 electron in CH_3S on Au(111),[14] and 0.22 electron in CH_3S on Co(0001) (Ref. 15) have been reported. This implies that an adsorbed CH_3S molecule is always negatively charged on the Cu(111) surface. Thus, an electrostatic attractive or repulsive force (depending on the polarity of the tip) is generated in an STM junction by the local electric field gradient and the negative charge on the molecule. However, for random hopping, the apex of the tip was positioned on the molecular center [Fig. 3(d)]. This means that the local electric field in an STM junction is approximately homogeneous parallel to the surface. Therefore, the hopping direction of a CH_3S molecule is not restricted by the electric field and as a result, the molecule hops randomly on the surface.

On the other hand, a repulsive force appears between the tip and the molecule when a negative bias voltage is applied to the STM tip [Fig. 3(e)], inducing the molecule to hop to the nearest-neighbor hollow site to move away from the STM tip. In contrast, the molecule is attracted toward a positively charged STM tip during the hopping [Fig. 3(f)], and prefers to hop to the site labeled in Fig. 3(c).[16] We also succeeded in controlling the hopping direction of an individual CO molecule on Pd(110) [Fig. 4(a) and 4(b)]. This
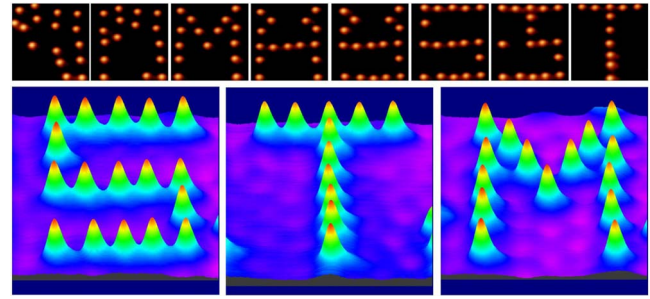

FIG. 5. (Color online) Sequential STM images showing the gradual construction of the letters and three-dimensional images of the letters S, T, and M with CH_3S molecules on Cu(111). Scan area for each image is 6×6 nm^2.

was achieved because the molecule can hop on the surface due to the excitation of molecular vibration by means of inelastic tunneling electrons[5] and the charge is transferred from the substrate to the molecule,[17,18] a mechanism that further supports the validity of our model. In the CO molecule on a Pd substrate, the typical magnitudes of the electric fields under the apex of the tip in an STM junction are estimated to be about 810 mV/nm for the attractive and repulsive hopping, respectively. Compared to the case of CH_3S molecule on Cu substrate, this magnitude is obviously large. In the case of CH_3S on Cu(111), a density-functional theory calculation of the adsorbed state shows a large electron transfer from the substrate to the adsorbate whereby the lowest unoccupied molecular orbital downshifts toward the Fermi level.[8] Although it has not been determined for certain about the magnitude of charge transfer from Pd substrate to CO molecule, it might be very small by the effect of electron back donation from the molecule to the substrate. Therefore, a large magnitude of the electric field would be needed to deliver precisely the CO molecule on the surface.

According to the proposed model, the controllability of the manipulation can be expected to drop as the electric-field gradient levels off. To test this, we changed the degree of the electric-field gradient (i.e., the gap resistance between the STM tip and the substrate) and measured the difference. In order to control the electric-field gradient in an STM junction in this experiment, the amount of tunneling current was varied for a constant bias voltage. By this means, we can reveal the effect of the electric field gradient on the controlled hopping probability. Here, P_{cont} is defined by the ratio between the number of controlled hopping events and that of trial events; that is, "$P_{cont}=1$" means that the percentage of controlled hopping is 100%. With a gap resistance of 25 MΩ (corresponding to the tip-surface distance ($d_{tip-surf}$) of 0.74 nm), $P_{cont}=1$ was obtained when a bias voltage of 200 mV is applied to the tip. However, with a gap resistance of 50 MΩ ($d_{tip-surf}=0.77$ nm), random hopping was observed despite the extraction of tunneling electrons from the off-center position of the molecule. A similar tendency was observed for repulsive hopping, that is, when the tip was negatively charged. When a bias voltage of −400 mV was applied to the tip, P_{cont} was 0.80 with a gap resistance of 60 MΩ ($d_{tip-surf}=0.78$ nm), and P_{cont} dropped to 0.65 with 400 MΩ ($d_{tip-surf}=0.86$ nm). With a gap resistance of 2000 MΩ

($d_{tip-surf}$=0.93 nm), P_{cont} was 0.33, which means the hopping was completely random. These results further support the validity of our proposed model.

The field-induced diffusions reported previously are caused by the interaction of the induced dipole moment[19] or intrinsically charged atoms[20] with the electric-field gradient at the surface. For the atoms or molecules in their ground state, a strong electric field of a few volts per nanometer is required for making them diffuse. The electric field necessary for these species is about ten times larger than that in our experiment, and therefore, we assume molecular hopping caused by field-induced diffusion is not dominant in the results presented here. Moreover, the sharp threshold at ±85 mV [Fig. 1(f)] implies that the vibrational excitation is the dominant cause of the hopping, and the weak electric field inhomogeneously applied to a molecule should determine the hopping direction.

This study reveals that a vibrationally excited molecule can be precisely positioned with the aid of a local electric field in an STM junction. A single molecule on a surface in a vibrationally excited state can respond to the electric field from an STM tip. In order to demonstrate the controllability, we fabricated an artificial structure, "S," "T," and "M," by inducing lateral hopping of CH_3S molecules on Cu(111) (Fig. 5). This noncontact process for manipulating and positioning individual molecules offers some advantages that are not provided by conventional manipulation such as rapid movement of molecules between two sites and the extremely low probability of the STM tip breaking or of molecular dissociation often caused by strong tip-molecule interaction.

*ykim@riken.jp

†maki@riken.jp

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[6] Typical conditions for obtaining STM images were V_{sample}= −20 mV and I_{tunnel}=0.2 nA. The $(CH_3S)_2$ vapor was exposed to the clean Cu(111) surface at a temperature below 50 K. CH_3S molecules were produced by the S-S bond dissociation reaction of isolated $(CH_3S)_2$ molecules, induced by the injection of tunneling electrons from the STM tip. During the reaction and the manipulation, the substrate was kept at 4.7 K.

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[11] Based on this assumption, we estimate that "*I*" is 2 nA, when "*d*" is 8 Å (i.e., *R* is 0.1 GΩ), and a bias voltage (*V*) of −0.2 V is applied to an STM tip to induce the attractive hopping. More-over, based on the tunneling current characteristic of STM, the value of "*I*" can be estimated as 0.2 nA, when d=9 Å and V =−0.2 V. Furthermore, "*I*" should be 0.02 nA, when d=10 Å and V=−0.2 V. Therefore, the tip-surface distance ($d_{tip-surf}$) is given by "$d_{tip-surf}$=8−log(*I*/2)=8+log 2−log *I*" for attractive hopping.

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