# Local chemical reaction of benzene on Cu(110) via STM-induced excitation

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We have investigated the mechanism of the chemical reaction of the benzene molecule adsorbed on Cu(110) surface induced by the injection of tunneling electrons using scanning tunneling microscopy (STM). With the dosing of tunneling electrons of the energy 2–5 eV from the STM tip to the molecule, we have detected the increase of the height of the benzene molecule by 40% in the STM image and the appearance of the vibration feature of the $\nu$(C–H) mode in the inelastic tunneling spectroscopy (IETS) spectrum. It can be understood with a model in which the dissociation of C–H bonds occurs in a benzene molecule that induces a bonding geometry change from flat-lying to up-right configuration, which follows the story of the report of Lauhon and Ho on the STM-induced change of benzene on the Cu(100) surface. [L. J. Lauhon and W. Ho, J. Phys. Chem. A **104**, 2463 (2000)]. The reaction probability shows a sharp rise at the sample bias voltage at 2.4 V, which saturates at 3.0 V, which is followed by another sharp rise at the voltage of 4.3 V. No increase of the reaction yield is observed for the negative sample voltage up to 5 eV. In the case of a fully deuterated benzene molecule, it shows the onset at the same energy of 2.4 eV, but the reaction probability is $10^3$ smaller than the case of the normal benzene molecule. We propose a model in which the dehydrogenation of the benzene molecule is induced by the formation of the temporal negative ion due to the trapping of the electrons at the unoccupied resonant states formed by the $\pi$ orbitals. The existence of the resonant level close to the Fermi level ($\sim$2.4 eV) and multiple levels in less than $\sim$5 eV from the Fermi level, indicates a fairly strong interaction of the Cu-$\pi^*$ state of the benzene molecule. We estimated that the large isotope effect of $\sim 10^3$ can be accounted for with the Menzel–Gomer–Redhead (MGR) model with an assumption of a shallow potential curve for the excited state.   © *2004 American Institute of Physics.* [DOI: 10.1063/1.1647044]

## I. INTRODUCTION

There has been a rising interest for inducing a chemical reaction in the nanoscale region with the use of a scanning tunneling microscopy (STM).[1,2] The tunneling electrons from the STM tip are spatially localized in an atomic scale area, and have a large current density of $\sim$1 MA/cm$^2$ that cannot be obtained easily by other conventional electron sources. It has been demonstrated that the tunneling electrons can induce electronic[3–5] and/or vibrational excitation[6–11] of the adsorbates that cause various surface phenomena. These studies can reveal the pathway to how the energy stored with such excitation is transferred to the chemical reaction of the molecules. In addition, they shed light on the electronic and/or vibrational structure itself, giving supplemental information to the spectroscopic data.

Moreover, the use of inelastic tunneling spectroscopy (IETS) for the chemical analysis is a candidate for the ultimate chemical analysis.[2] The combination of such features of STM can open a new area of chemistry; nonthermal control of surface phenomena induced by the dosing of electrons into surface adsorbates.

Recently Lauhon and Ho have shown the experiment of tunneling-current-induced reaction of the benzene molecules on Cu(100) with combining a STM observation and the IETS measurements.[12] There the C–H bond breaking occurs by the electron dosing into the molecule followed by the bonding configuration change from flat-lying to up-right. Inspired by the above paper, we investigate in the current paper the detail of the mechanism of the chemical reaction of a benzene molecule adsorbed on Cu(110) caused by the dosing of tunneling electrons. Similar experiments were performed on benzene molecules on the Si surface,[13,14] but the current experiment gives quite different behavior of benzene molecules.

We have confirmed that the chemical reaction of the benzene molecule is also induced on Cu(110) by the injection of tunneling current by using the STM images and the IETS measurement. There we have found the multiple voltage onsets for the increase of the reaction at $\sim$2.4 and $\sim$4.3 eV, which apparently corresponds to the resonant level formed by the $\pi^*$ state of the benzene molecule. The existence of a $\pi^*$ originated state close to the Fermi level ($\sim$2.4 eV) deviates from the model of the weak interaction between the Cu and the benzene molecule, but coincides well with the recent XAS experiment on the benzene molecules on Cu(110).[15] There is no increase of the reaction yield in the occupied state, which indicates that the phenomenon is induced by the formation of the tentative negative ion. In addition, there is a large isotope effect on the reaction yield; the yield of the fully deutrated benzene molecule is $10^3$ times smaller than that of the normal benzene. It is shown that the large isotope effect can be explained with the framework of the Menzel–

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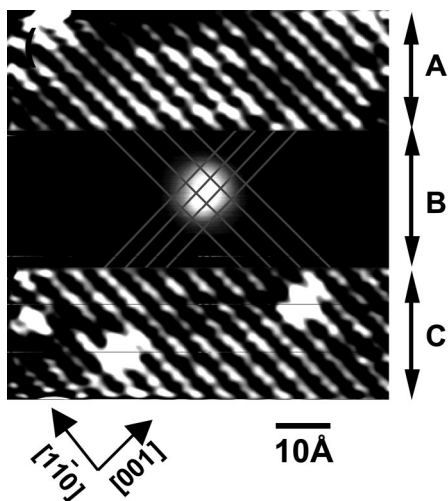
FIG. 1. (a) STM topographic image of the benzene molecule adsorbed on Cu(110) at 4.7 K (area 72×72 Å$^2$). The observation conditions are $V_{sample}$ =2 mV and $I_{tunnel}$=15 nA in the upper (A) and lower (C) portion of the panel, are $V_{sample}$=500 mV and $I_{tunnel}$=0.5 nA in the middle portion (B).
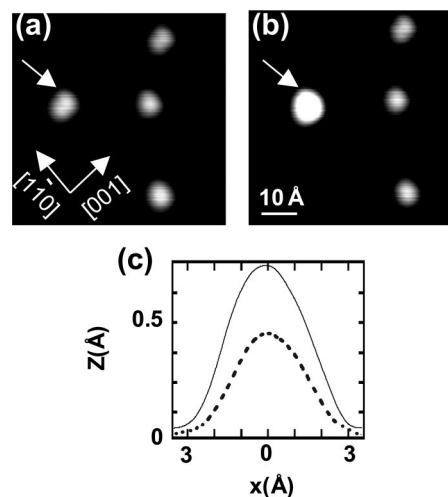


FIG. 2. (a), (b) Topographic image of the molecules of benzene and its reacted product. The observation conditions are the tunneling current of 0.6 nA, the sample bias voltage of −500 mV, and the area of 43×43 Å$^2$. The target molecule of benzene is shown by the arrow in (a), which becomes brighter at the arrow in (b) by the dosing of tunneling electrons with the energy of 4 eV (sample bias positive) for 0.2 s. (c) Cross section of the images of the benzene molecule (dotted line) and its reacted product (solid line). The height of the reacted product is 44% greater than that of the benzene molecule.

Gomer–Redhead (MGR) model by assuming a shallow potential curve for the negative ion state.

## II. EXPERIMENT

A clean Cu(110) surface was prepared by the standard cleaning technique with repetitive Ar$^+$ sputtering and annealing cycles. The benzene 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.[8,10]

The STM-IETS measurement is carried out as follows: the STM tip is precisely positioned over a target molecule and the feedback loop is then turned off. The sinusoidal modulation of 397 Hz in frequency and 5.7–14.1 mV$_{rms}$ in amplitude is superimposed on the sample bias voltage, $V_s$. The second harmonic of the modulation frequency was measured with a lock-in amplifier, which is proportional to $d^2I/dV^2$ (a derivative of the ac tunneling conductance), which exhibits a peak-shaped signal at the threshold energy for excitation of the vibrational mode. The signals are collected and averaged after each bias scan.[10]

## III. RESULTS AND DISCUSSION

A typical topological STM image of the Cu(110) surface is shown in Fig. 1, where isolated benzene molecules can be observed as protrusions with a circular shape. In the image of Fig. 1, we intentionally reduce the gap distance in the area without the benzene molecules, and increase the gap distance in the area that contains the molecule; the reduced gap distance can give an atomic structure of the substrate and the widened gap distance minimizes the tip–molecule interaction that disturbs the observation of the bonding position of the molecule. This gives the atomic position of the substrate and the position of the molecule within a single image.

The areas marked A and C are imaged with the sample bias of 2 mV and the tunneling current of 15 nA, while the image in the area B is obtained with the conditions of 500 mV and 0.5 nA. The grid is formed based on the atom positions of the substrate in the areas A and C, in which the lattice points correspond to the atomic position of the Cu atoms.

The center of the circular image of the benzene molecule is located at the center of the rhombic, indicating that the molecule is adsorbed at the hollow-site position. The observed position is identical with the report of Doering, in which it was claimed that the benzene molecule occupies the hollow site with the benzene ring being parallel to the surface.[16] In addition, there is a theoretical calculation that supports the flat-lying and hollow-site bonding configuration of the benzene molecule on the Cu(110) surface.[17]

When tunneling electrons are dosed on the benzene molecule, the apparent change of the height of the molecule occurs. An example of such a change is shown in Fig. 2, in which equivalent four benzene molecules are observed in the initial image shown in Fig. 2(a) and the single molecule marked by an arrow is the target molecule. After the dosing of the electrons only on the target molecule, which are injected for 0.2 s with the bias voltage of 4.0 V and the feedback loop being off, the target molecule apparently changes its height and becomes brighter than other intact benzene molecules [Fig. 2(b)]. As shown in the cross section image in Fig. 2(c), the height of the molecule is changed from 0.49 ±0.04 to 0.71±0.06 Å. At this stage we can speculate that a chemical reaction occurs at the target benzene molecule and its height is increased.

In order to execute chemical identification on the molecule before and after the tunneling electron dosing, we per-
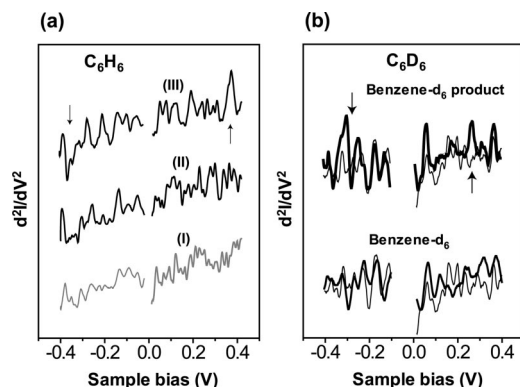
FIG. 3. (a) Vibrational spectra ($dI^2/dV^2$ vs $V$ plot) obtained on the clean Cu(110) surface (I), the benzene molecule (II), and its reacted product (III) by STM-IETS taken at a gap resistance of 1 GΩ and $V_{rms}=5$ mV modulation at 398 Hz. The spectra are the averages of 20 scans for the bias range between −0.4 and 0.4 V. (b) STM-IETS spectra on the deutrated benzene molecule ($C_6D_6$) and its reacted product. On both spectra, the spectrum on the Cu substrate is superimposed by a thin line.
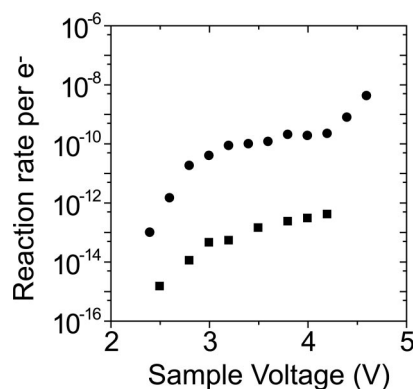


FIG. 4. Reaction yield per electron for $C_6H_6$ and $C_6D_6$ molecules as a function of the sample bias voltage of the injected electrons. The data were sampled over 180 benzene molecules.

form the measurement of the inelastic tunneling spectroscopy (IETS).

Figure 3(a) shows the comparison of IETS spectra obtained on the Cu(110) substrate (I), on the benzene molecule (II), and on the benzene molecule after the dosing of the tunneling electrons (III). Three spectra are obtained using the same tip, and the overall structures are well reproduced in all spectra. The most prominent feature observed on the molecule is the one at the energy of 372 meV and −380 mV in the spectrum (III) obtained on the reacted product of the benzene molecule. The positions are marked by arrows, at which positions no noticeable features can be seen neither in the substrate Cu(110) spectrum nor on the benzene molecule spectrum. The energy of the tunneling electrons is in the range of the vibrational energy of the C–H stretching mode. The spectra for the deuterated benzene molecule are plotted in Fig. 3(b), in which the comparison of the spectra before and after the electron dosing is shown with the substrate spectrum being superimposed. Deuteration of the molecule causes the energy shift of this peak to 275 and −282 mV, which is also observed only on the reacted product. The energy positions of the $\nu$(C–H) mode for the normal benzene and the deuterated benzene have been reported as 378 and 282 mV, respectively, on the Cu(100) surface by STM-IETS.[12] These observation indicates that the $\nu$(C–H) vibrational mode appears only after the dosing of the tunneling current on the benzene molecule.

The behavior of the benzene molecule with the dosing of the tunneling electrons, which have been shown above by the change of the height of the molecule in the STM image and the vibration features in IETS spectra, is basically identical with the one of the benzene molecules on Cu(100) reported by Lauhon and Ho.[12] In that paper, they compared the spectra of pyridine and benzene molecules, which are known to have up-right and flat-lying bonding configuration, respectively. They concluded that the benzene molecule change its bonding configuration from the flat-lying to the up-standing by the dosing of the tunneling current, in which process the hydrogen atoms of the benzene molecule are detached. We

therefore understand our results in the same scenario with the one on a Cu(100) surface; the C–H bond breaking is induced by the tunneling electrons to form $C_6H_4$ or $C_6H_5$.

We often observe a dark area near the benzene molecule to which tunneling electrons are dosed and the possible dehydrogenation occurs. The image of the dark area resembles the one for the hydrogen atoms adsorbed on the Cu substrate.[18] We consider that the dark area indicates the position of the H atom that is dissociated from the benzene molecule and recombined with the Cu substrate.

In order to understand the mechanism of the chemical reaction of the benzene molecule, we systematically measure the reaction probability by changing the conditions for the dosing of tunneling electrons both for the normal benzene molecules and the deuterated benzene molecules.

First we have measured the reaction probability per electron as the function of the sample bias voltage with the fixed current of 1 nA in Fig. 4, where the vertical axis is shown in log scale. For the normal benzene molecule, the reaction probability shows a rapid increase at ~2.4 eV, which is apparently saturated at ~3.0 V. The curve shows another intriguing increase of the reaction probability at ~4.3 eV. For the deuetrated molecule, the curve shows the increase at ~2.4 eV like the normal benzene molecule. However, the absolute value of the probability is ~$10^3$ smaller at the plateau in the deuterated case compared to the normal benzene molecule. The curve shows no increase of the reaction probability in the negative sample-bias region up to ~5 eV, both for the normal and the deuterated benzene molecules. Lauhon and Ho claimed that the onset voltage of the benzene fragmentation is 2.9 V for the normal benzene molecule and 4.4 V for the fully deuterated molecule. We consider the latter threshold for deuterated benzene corresponds to the second rise of the probability in the current report, which is due to the small probability for the deuterated molecule.

Next, we show the reaction probability in the unit time period as the function of the tunneling current. The results obtained for the normal benzene and the deuterated benzene molecule are shown in Figs. 5(a) and 5(b), respectively. The bias voltage of the tunneling electrons is fixed at 4 eV. The linear line in the graph corresponds to the results of the fit-
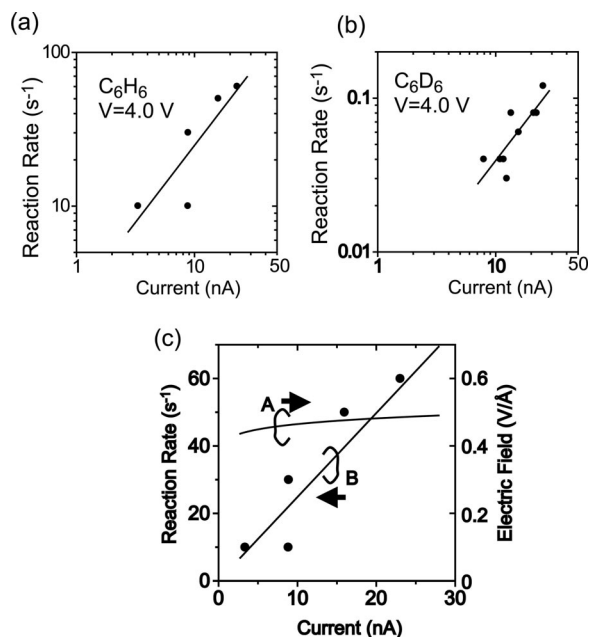
FIG. 5. Reaction rate of $C_6H_6$ (a) and $C_6D_6$ (b) molecules by the injection of tunneling electrons with the energy of 4 eV (sample positive bias). The reaction rate is plotted as a function of the tunneling current, and both *x* and *y* axis are shown in long scale. The lines in both graphs correspond to the result of the linear fit using the least square method, where the slopes are calculated to be 1.00 for both cases. (c) The curve A corresponds to the variation of the estimated electric field between the tip and the sample (see the text). The dots and the line B indicate the reaction rate versus the tunneling current, whose data are identical with the one in (a) but are shown in the linear scale.

ting with the least square method, where the slope is determined to be 1.0 for both cases.

If we assume that the reaction is induced solely by the tunneling electrons, the reaction probability *P*, the current *I*, and the reaction order *n* should have the relation of $P = I^n$. Thus, it is deduced that the reaction order is ~1 from the above fitting, and thus the phenomena is a one-electron process.

As one of the candidates for the chemical reaction, we should consider the electric field formed by the tip and the substrate. In the measurement shown in Fig. 5, the tunneling gap is adjusted so as to make the tunneling current constant. Thus, the electric field should show complex behavior when the bias voltage is increased. We assume that the decrease of the gap distance by 1 Å makes the tunneling current increased ten times, and the gap distance of the metal surface observation $d \sim 8$ Å with the tunneling resistance of 0.1 GΩ.[19] The simplified parallel plane model forms the electric filed $E$ (V/Å) with the following formula; $E(I) = 4/8 - \log(I/40)$. The behavior of *E* vs *I* is like the curve A shown in Fig. 5(c). The nonlinear behavior shows quite a difference from the experimental data of the *P* versus *I* curve. Thus, we diminish the effect of the electric field for the chemical reaction as the primary mechanism. Instead we consider the dehydrogenation is induced by the electron dosing into the molecule.

Here we examine the origin of the characteristic features in the C–H breaking yield versus the *V* curve shown in Fig. 4; namely the multiple onset voltages and the large isotope

effect for the reaction yield. First we examine the onset of the reaction probability identified at ~2.4 eV. One might argue that the energy coincides with the energy of the barrier for the C–H breaking in this system. In the case, the energy of the tunneling electron is totally transferred for the C–H bond breaking. The thermal behavior of the C–H breaking from the benzene molecule has been studied previously on an Ag(110) surface.[20] It was observed that the C–H bond breaking commences at the temperature of ~320 K. Though the accurate activation energy cannot be deduced solely from this measurement, we can roughly estimate that the activation energy of the C–H breaking is in the range of ~1.0 eV. Though there is no experimental data for Cu(110) as far as we know, we speculate that there should be no large difference in the chemical reactivity for the surfaces of Ag(110) and Cu(110). Thus, the onset at the energy of ~2.4 eV does not likely correspond directly to the activation barrier for the C–H bond breaking.

The next possibility is that these energies coincide with the molecule-induced resonant levels in the unoccupied state. The surface chemical reactions are induced either by tunneling electrons being directly tunneled into these states forming temporary ions or excited electrons into these states. Examples can be seen in the CO desorption from the Cu(111) surface,[21] and Si–H bond breaking[22] for the former and the latter case, respectively. We speculate that there are multiple molecule resonant states in the unoccupied state in benzene on the Cu(110) case.

It has been considered that the electronic interaction between the Cu surface and the benzene molecule is weak and the energy level of the LUMO state is close to the one of the benzene molecule in the condensed phase. The idea is supported by the observation using the inverse photoemission spectroscopy and two-photon photoemission spectroscopy of the benzene molecule adsorbed on the Cu(111) surface and the $e_{2u}$ state is assigned at ~4.6 eV above the Fermi level.[23,24] The energy is much higher than the onset of ~2.4 eV observed in the current experiment. However, the electronic state revealed by the x-ray emission spectroscopy (XES) is much different for the benzene molecules adsorbed on Cu(110).[15] Molecule-induced sharp features can be identified at the energies very close to the Fermi level in the unoccupied state. They are assigned as the antibonding and bonding state formed by the hybridization between the benzene $e_{2u}$ state and the valence orbitals of the Cu. In addition, due to the symmetry breaking with the upward flipping of the C–H bond, there exist multiple states in the energy levels less than ~5 eV. These findings indicate a fairly strong interaction between the Cu and the benzene molecule. The observation is consistent with our finding of the low onset energy for the reaction probability and the apparent multiple resonant states in the energy region less than 5 eV above the Fermi level. Since no significant increase of the reaction yield up to 5 eV in the occupied state, we believe that this phenomenon is caused by the negative ion formation by the temporal trapping of the tunneling electrons.

Next, we examine the observed isotope effect on the reaction yield between the normal and the fully deuterated benzene molecule; the ratio is ~$10^3$, as can be seen in Fig.

4. In the experiment of the H desorption from Si surface using STM, the isotope effect on the dehydrogenation probability is also observed; ~50 times higher for the H desorption compared to the D desorption.[3,22] The mechanism has been understood with the Menzel–Gomer–Redhead (MGR) model,[25] the tunneling electrons contribute to the electronical excitation from the $\sigma$ state to the $\sigma^*$ state that are the Si–H bonding state and the antibonding state, respectively.

After the electron excitation occurs, the motion of the H atom follows the potential energy surface (PES) of the $\sigma^*$ state, in which the potential energy is monotonically lowered with the extension of the Si–H distance and leads to the Si–H dissociation without any barrier. Even if the quenching from $\sigma^*$ to $\sigma$ occurs before dissociation, the dissociation can be accomplished in case ample kinetic energy is already stored. Thus, the critical Si–H distance, $d_c$, can be defined at which the H atom has gained the kinetic energy that is equal to the activation barrier for the dissociation. If the quenching occurs before the Si–H distance reaches $d_c$, the H atom returns to its original position; the dissociation occurs if no quenching occurs before reaching $d_c$. The isotope shift of the dehydrogenation of the Si–H surface has been attributed to the different kinetic behavior of the hydrogen and the deuterium atoms. The deuterium atom, because of its heavier mass, experiences about one-half the acceleration of hydrogen. If the time required for the H atom to reach $d_c$ is defined as $t_c$, then it is $\sqrt{2}t_c$ for D. At that time the amplitude of the wave packet of Si–D is reduced to be $\exp(-\nu(\sqrt{2}-1)t_c)$ from that of Si–H, where $\nu$ is the quenching rate.[22] Avouris and Persson have shown quantum chemical analysis and deduced a result to account for the experimental results of the isotope effect of ~50.[22]

We want to apply this analysis to our current system to examine whether the isotope effect of $\sim 10^3$ in the reaction yield can be explained in the MGR model.

For that analysis, we have to know the shape of the PES (especially the activation barrier for the dissociation and the slope of the potential in the excited state) and the quenching rate in the excited state. Though data have not been obtained explicitly for the system of benzene on the Cu(110) surface, we want to make a rough estimation of the expected isotope effect from the known results on the excited state. Chen *et al.* have deduced the lifetime of the excited state on the benzoate on Cu(110) is ~1.1 fs.[26] The activation barrier is deduced from the thermal behavior of the benzene molecule on Ag(110), which is roughly ~1 eV.[20] To account for the observed isotope effect of $\sim 10^3$, the expected slope of the excited state is 0.89 eV/Å. The value corresponds to a shallow potential, but within a reasonable range. A combination of the desorption experiment with the STM tip and the two-photon photoemission spectroscopy, Bartels *et al.* have estimated that the slope of the potential curve of the $2\pi^*$ state is 1–4 eV/Å and the lifetime of 0.5 fs for CO on Cu(111).[21]

Finally, we want to mention on the path how the occupation of the $\pi^*$ state induces the C–H bond breaking. The $\pi^*$ state is composed of $p$ orbitals perpendicular to the plane of the benzene molecule, which is not directly related to the C–H bonding. One possibility for the connection of the occupation of the $\pi^*$ state to the C–H bond breaking is the broken symmetry of the benzene molecule upon absorption; the flipping C–H bond may makes the mixing between the $\pi^*$ orbital and the electronic state at C–H.

In addition, the desorption of the benzene molecules were observed in the hole resonant state (holes in the $\pi$ state) on the Si surface and not in the electron resonance.[13] Such differences should be examined by theoretical calculation to understand the dynamics of the excited state into chemical reactions.

## IV. SUMMARY

As a summary, we have examined the mechanism for the tunneling electron-induced chemical reaction of benzene molecules on Cu(110). The benzene molecule, which is initially located at the hollow site with a possibly flat-lying configuration, shows an increase of the height in the image by ~40%. In addition, the vibrational feature of the $\nu$(C–H) mode is detected on the benzene molecule only after the injection of the tunneling electrons at the sample biases of 372 and −382 mV, and at 275 and −282 mV for the deuterated benzene molecule. This behavior is identical with the ones reported for the benzene molecules on Cu(100). As has been reported in that report, it is apparently that C–H bond breaking occurs on the benzene molecule with the dosing of the tunneling current, which makes the bonding configuration change from flat-lying to up-right. We investigate the relation between the reaction probability and the energy of the dosed electrons. The reaction probability shows the onset voltage at 2.4 and 4.3 V in the sample-positive region, but not detected in the sample-negative region. The deuterated benzene also shows the onset voltage at 2.4 V, but the probability is $10^3$ smaller than that obtained on the normal molecule. The curve fitting of the reaction probability versus the tunneling current shows it is a one-electron process. We consider that the C–H bond breaking is induced by the temporal negative ion formation, which is formed by the trapping of the tunneling electrons at the resonant levels of the molecule. The existence of the resonant level close to the Fermi level (~2.4 eV above the Fermi level) and the multiple resonant states within 5 eV from the Fermi level indicates a fairly strong electronic interaction between the Cu surface and the benzene molecule and agree well with the recent report with the method of the XAS. The large isotope effect appearing in the reaction yield of $10^3$ is analyzed with the MGR model; the model can account for the number if a shallow potential curve in the excited state is assumed.

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