

Tunneling spectroscopy and manipulation of a single C₂H₂ molecule on a Cu(111) surface

Yasuaki Konishi, Yasuyuki Sainoo,* Ken Kanazawa, Shoji Yoshida, Atsushi Taninaka,
Osamu Takeuchi, and Hidemi Shigekawa†

Institute of Applied Physics, 21st century COE, CREST-JST, University of Tsukuba, Tsukuba, 305-8573, Japan

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The adsorption structure of a single C₂H₂ molecule on a Cu(111) surface was analyzed by scanning tunneling microscopy (STM) and inelastic tunneling spectroscopy (IETS). The STM result showed a twofold rotational symmetry, in agreement with the structural model previously proposed. The IETS spectrum measured near a monatomic step exhibited peaks related to the C-H stretch mode, which were as strong as what had been reported for C₂H₂ on a Cu(100) substrate, where the amplitude of the electronic standing wave that causes background fluctuation of spectra could be considerably reduced by the reduction of scattering at the step. Chemical reactions induced by electron injection were also observed by IETS analysis near steps.

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The control and analysis of chemistry at the single-molecule level is a key to future nanotechnology and related applications in various fields, and its recent progress has been considerable.^{1–12} Inelastic tunneling spectroscopy (IETS) is a promising technique for these purposes, because of its high potential for the identification and manipulation of selected single-vibration modes.^{3–12} Due to the basic importance and broad catalytic applications in various fields, extensive studies have been performed on the chemical reactions of hydrocarbons on transition metals. Among them, C₂H₂ is an important molecule from fundamental and practical points of view. Pioneering works have been performed on Cu(100), Ni(100), Ni(110), and Pd(111) surfaces.^{3,9,10,13} An interesting characteristic is that the adsorption structure and molecular conformation vary depending on the surface, resulting in the differences in the STM image and in the IETS spectrum of single molecules. However, the obtained results are rather complicated. For example, on a Ni(110) surface, from the observation of two different sizes of circular C₂H₂ STM images and two associated C-H stretch modes in IETS spectra, at 368 and 357 meV, two different conformations of the C₂H₂ molecule (*sp*²-like and *sp*³-like) were found to exist.¹⁰ These characteristics are different from those on a Ni(100) surface, where a single dumbbell-like STM image and a 360 meV IETS peak were observed.⁹ On Cu(100) surfaces, a single C-H stretch mode and dumbbell-like STM image were confirmed, similar to those on a Ni(100) surface, but the stretch mode was 357 meV.⁹ The molecular plane was tilted on a Pd(111) surface and an asymmetric STM image was observed.¹³ On a Cu(111) surface, the C₂H₂ molecule is considered to be adsorbed with its plane perpendicular to the surface, similar to that on a Cu(100) surface, but different from that on a Pd(111) surface. Since the molecular conformation strongly influences chemical reactions, a detailed understanding of the adsorption structures and reaction processes at the single-molecule level is extremely important.

To advance the research, we investigated the C₂H₂ molecule on a Cu(111) surface by STM and IETS. As mentioned above, despite the necessity of analysis at the single-molecule level, tunneling spectroscopy of adsorbates on a Cu(111) surface has not yet been performed adequately. We

speculate that this is mainly because of the difficulty in the spectroscopy measurement due to the strong influence of the standing wave of the surface state on the spectra. Namely, as shown by Crommie *et al.*,¹⁴ a surface-state band, whose parabolic dispersion relation has its minimum at ~ 0.5 eV below the Fermi level, contributes to the strong electronic standing wave at the energy levels near the Fermi level. Since the steps and defects on the surface act as scatterers of two-dimensional electrons, the standing wave has its fixed end at such local structures and gradually decays with distance from them. Since its decay length is very long, the standing wave often extends over almost the entire surface area. Since the wavelength of the standing wave is a function of the energy level, when a spectroscopic measurement is performed by STM, the phase of the standing wave at the measurement location changes as the measured energy level changes. This also causes the density of states to fluctuate largely there and, as a result, large background fluctuation arises in STS or IETS measurement. Consequently, no successful IETS measurement on Cu(111) substrate has been reported to date.

According to the analysis presented above, we derived a strategy for avoiding the strong effect of the standing wave. The key issue is that the phase of the standing wave at the surface step is almost fixed and the density of states for the surface state is also very low. Thus, the measured spectra near the step edge should be much less influenced by the standing wave. By this strategy, we succeeded in measuring the C-H stretch mode of a single C₂H₂ molecule adsorbed on a Cu(111) surface. The intensity of the C-H stretch mode in the spectra was comparable to that measured on Cu(100) surfaces, making it possible to analyze the tip-induced chemical reaction of a single C₂H₂ molecule on the surface. In this paper, we show our results for the tunneling spectroscopy and manipulation of a single C₂H₂ molecule on a Cu(111) surface.

The Cu(111) surface was prepared by several cycles of Ar ion sputtering and annealing at 820 K. The base pressure was 4.0×10^{-9} Pa. After confirming that the Cu(111) surface was clean, the STM tip was retracted from the sample and acetylene gas of $\sim 99\%$ purity was introduced through the variable leak valve below 10 K.

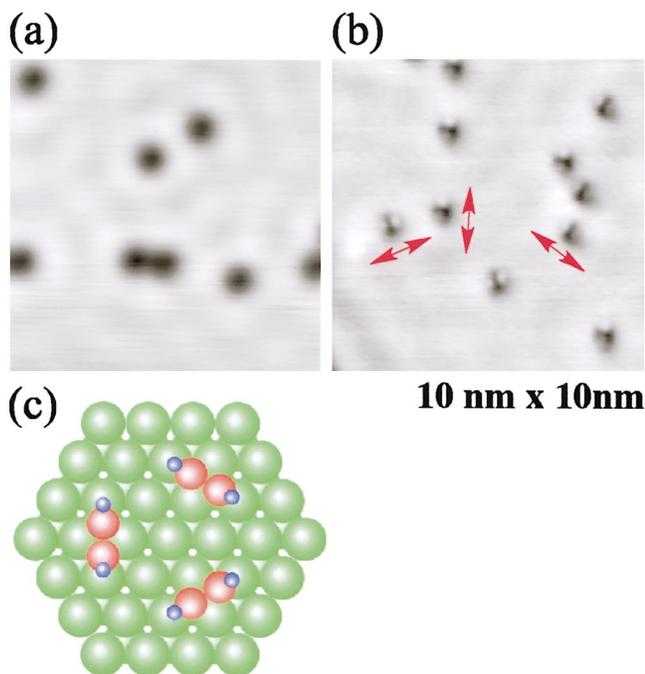


FIG. 1. Typical STM images of isolated C_2H_2 molecules on a Cu(111) surface ($10 \times 10 \text{ nm}^2$, +0.1 V, 1.0 nA) (a) and its high-resolution image obtained by a molecule-modified STM tip ($10 \times 10 \text{ nm}^2$, +0.5 V, 1.0 nA) (b). (c) Predicted model of the adsorption site. Green, silver, red, and purple circles indicate Cu, Pd, C, and H atoms, respectively.

Figure 1(a) shows a typical STM image of isolated C_2H_2 molecules on a Cu(111) surface. In general, C_2H_2 molecules are imaged as a dip with a simple round shape on the surface, however, they are sometimes imaged with higher resolution as a dumbbell-like shape, as shown in Fig. 1(b). This is probably caused by the modification of the tip apex by another C_2H_2 molecule, as previously reported in the case of STM observation of a CO molecule on a Cu(111) surface.¹⁵ In the high-resolution image, molecules in three orientations are observed, each of which rotated 120 deg relative to the others, reflecting the threefold symmetry of the Cu(111) substrate.

A magnification of the high-resolution image and the schematic model of the corresponding molecular conformation proposed in the previous experimental and theoretical studies are shown in Fig. 2(a). Since the molecular plane is perpendicular to the surface, the adsorbate has twofold rotational symmetry. The corrugation between small white dots in the STM image is attributed to the backbond between the carbon and copper substrate, while two dips suggest that some charge transfer occurs from the Cu atom at these positions to the C_2H_2 molecule, the same as in the case of C_2H_2 adsorption on Cu(100).³ Indeed, as shown in Fig. 2(b), the situation is very similar in these two systems, except for the slight difference in the distance between the two dips in the STM image. This difference between the STM images of Figs. 2(a) and 2(b) reflects the symmetry of the substrate. When the molecule is tilted, the situation is very different, as in the case of the C_2H_2 adsorption on Pd(111) shown in Fig. 2(c).¹³ The asymmetry in the molecular conformation is

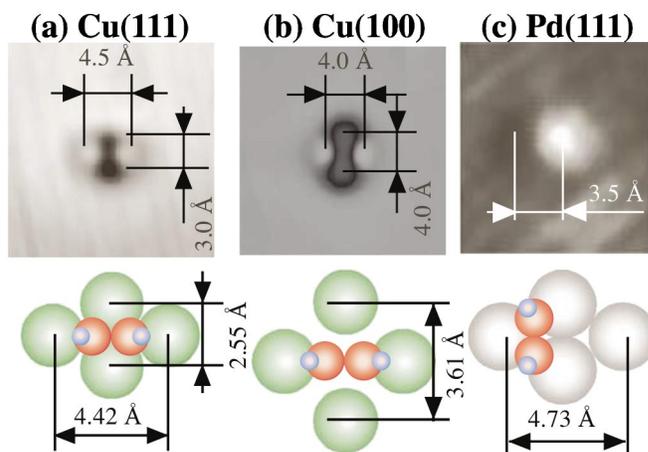


FIG. 2. (a) Magnification of the high-resolution image in Fig. 1(b). For comparison, STM images of a C_2H_2 molecule on Cu(100) and Pd(111) surfaces and their schematic models are also shown in Figs. 2(b) and 2(c), respectively. The imaging conditions of (a), (b), and (c) were (+1.0 V, 1.0 nA), (+100 mV, 10 nA), and (+40 mV, 400 pA), respectively. All images area is $25 \times 25 \text{ \AA}^2$. Green, silver, red, and purple circles indicate Cu, Pd, C, and H atoms, respectively.

strongly affects the symmetry of the STM image. Overall, our STM observation strongly supports the previously proposed structural model for C_2H_2 on Cu(100).

Next, we present IETS spectra obtained on the bare Cu(111) surface. As mentioned earlier, on the Cu(111) surface, the standing wave of the surface state strongly influences the tunneling spectra due to the change in the wavelength with the change in the bias voltage during the measurement. Figure 3 shows typical IETS spectra obtained near a step (\star) and at a terrace, $\sim 20 \text{ nm}$ from a step edge (\blackstar). As expected from the dispersion relation of the surface state,¹⁴ the signal in the spectrum begins to oscillate significantly with bias voltage V_t above $\sim -0.5 \text{ V}$ which is the bottom of the band, and is smooth for $V_t \lesssim -0.5 \text{ V}$. The influence is stronger at a terrace (\blackstar).

The spectra presented in Fig. 3 exhibit many peaks and dips although the measurement was carried out on the bare substrate. We emphasize that these structures in the spectra are highly reproducible. For example, two IETS spectra obtained for the same position under slightly different tip-sample separation distances are shown in Fig. 3(c) by blue and red lines. The spectra are almost identical, except for the slight difference in intensity. The random noise component, which is given by the difference between the two lines, has as low an intensity as the fluctuation of the baseline of an IETS spectrum measured on a substrate without a strong standing wave, such as the Cu(100) substrate (shown by green line). Since the interference effect is strong around the signal position of the C-H stretch mode measured by electron energy loss spectroscopy (EELS) (362 mV),¹⁶ it is difficult to identify the signal in the spectrum at a terrace.

Solid curves in Fig. 4(a) show typical IETS spectra obtained for the C_2H_2 molecules in Fig. 4(b) (T and S). Dotted curves are spectra obtained for the bare surface near T and S .

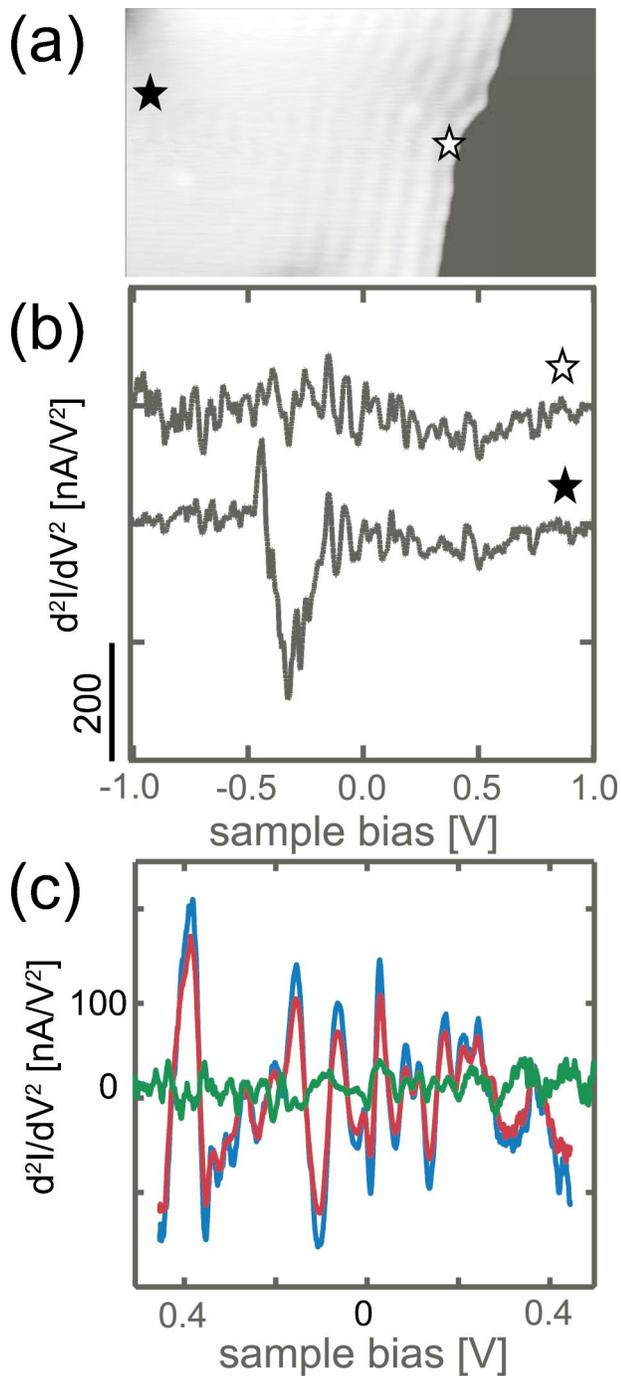


FIG. 3. (a) STM image ($27 \times 15.5 \text{ nm}^2$, $+80 \text{ mV}$, 1.0 nA) and (b) IETS spectra of Cu(111) surface obtained near (☆) and $\sim 20 \text{ nm}$ from (★) a step edge. Set point conditions are $Vt = +80 \text{ mV}$, $It = 1.0 \text{ nA}$. Modulation and time constant during the lock-in measurement are $\Delta V = 7 \text{ mV}$ at 794.7 Hz and $\tau = 100 \text{ ms}$, respectively. Signals were integrated 16 times. (c) Comparison of IETS spectra obtained on (100) (green, $Vt = +80 \text{ mV}$, $It = 1.0 \text{ nA}$, $\Delta V = 7 \text{ mV}$ at 766.6 Hz , $\tau = 100 \text{ ms}$, eight times integrated) and (111) surfaces (blue, $Vt \leftrightarrow +60 \text{ mV}$, $It = 1.3 \text{ nA}$, $\Delta V = 10 \text{ mV}$ at 333 Hz , $\tau = 100 \text{ ms}$, eight times integrated; red, $Vt = +80 \text{ mV}$, $It = 1.5 \text{ nA}$, $\Delta V = 12 \text{ mV}$ at 333 Hz , $\tau = 100 \text{ ms}$, eight times integrated).

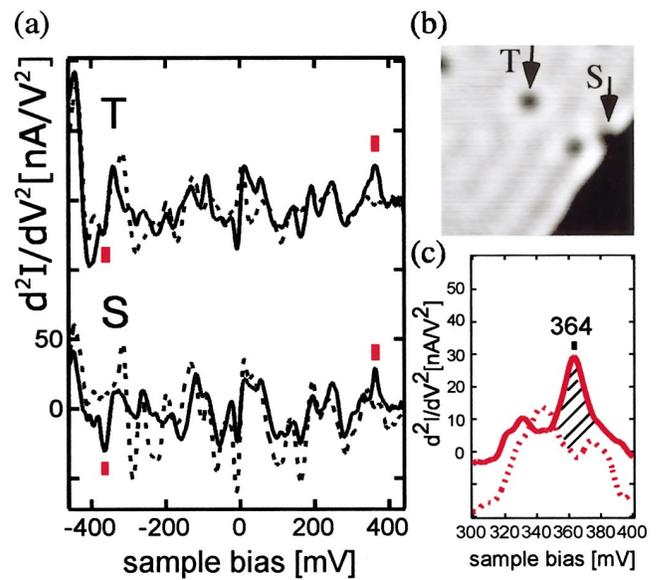


FIG. 4. (a) IETS spectra obtained over C_2H_2 molecules [T and S in (b)], scale, $8.7 \times 8.7 \text{ nm}^2$ near a step edge. (c) Schematic for the calculation of IETS intensity. ($Vt = +80 \text{ mV}$, $It = 1.0 \text{ nA}$, $\Delta V = 7 \text{ mV}$ at 336 Hz , $\tau = 100 \text{ ms}$, 16 times integrated). Red marks in (a) indicate the positions of signals at $\pm 364 \text{ mV}$. Dotted curves are the spectra obtained for the bare Cu surfaces near T and S in (a).

The difference between the solid and dotted curves represents the molecule-specific feature, in addition to the small difference in the standing-wave corrugation due to the slight difference in the measurement position and the scattering effect of the molecule itself. There exist peaks at $\pm 364 \text{ mV}$ from the C_2H_2 molecule in both cases, as indicated by red marks the -364 mV peak is not yet clear in the spectrum obtained for T , although $\pm 364 \text{ mV}$ peaks are clearly observed in the spectrum obtained just near the step edge (S), as expected.

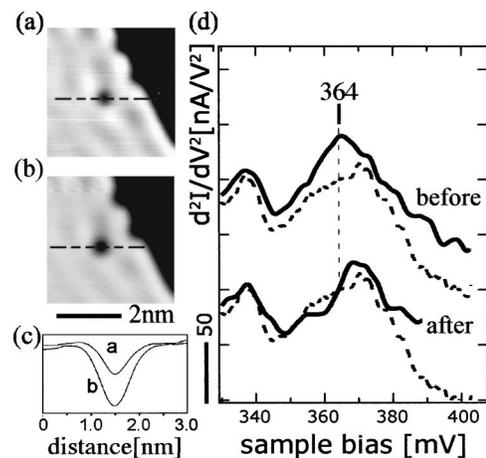


FIG. 5. STM images before (a) and after (b) applying a voltage of $+3.0 \text{ V}$ for 10 sec . (c) Cross sectional STM images of the C_2H_2 molecules in (a) and (b), (d) IETS spectra of the molecules shown in (a) and (b). ($Vt = +80 \text{ mV}$, $It = 1.0 \text{ nA}$, $\Delta V = 10 \text{ mV}$ at 327 Hz , $\tau = 100 \text{ ms}$, 16 times integrated). Dotted curves are the spectra obtained for the bare Cu surfaces near the molecule in (a) and (b).

Next, let us compare the peak energies and intensities of the C-H stretch mode measured by IETS for the C_2H_2 molecules on the Cu(111) and Cu(100) substrates. The peak energy of 364 mV obtained by our measurement is slightly different from that on Cu(100), 358 meV. According to the results of previous studies,^{17,18} the bond angles of C-C-H for C_2H_2 on the Cu(111) and Cu(100) substrates are 116 and 150 deg, respectively. A conformational change from the sp^2 - to the sp^3 -like structure is assumed to cause the observed shift in energy level. The intensity of peaks in IETS spectra can be compared on the basis of the relative change in the differential conductance: $\Delta(dI/dV)/(dI/dV)$, as suggested in Ref. 11. Here, $\Delta(dI/dV)$ can be obtained by integrating the difference between two IETS spectra obtained on (solid line) and off (dotted line, considered as a background) the molecule, as shown by the hatched area in Fig. 4(c). The values were 6.6% and 12.7% for Cu(111) and Cu(100) surfaces, respectively. To clarify the difference in detail, further study including the selection rule, which has not yet been established, is necessary.

The peak intensity is sufficiently strong for the Cu(111) surface, which enables us to analyze chemical reactions on this surface. Since adsorption structures may influence the chemical reactions, comparison of required conditions on different surfaces is important. Figures 5(a) and 5(b) show the STM images before and after the reaction. Here, the reaction was induced by tunnel electron injection into the molecule with a bias voltage of +3.0 V for 10 sec. The circular dip corresponding to the molecule became slightly wider and deeper, as shown by the line profiles in Fig. 5(c), which were

measured along the broken lines in the STM images. We confirmed that bias voltage higher than 2.8 V was required for the reaction. A similar experiment has been performed for the C_2H_2 adsorbate on Cu(100),¹² the experimental result which was almost the same as what we described here. The authors of the paper interpreted the reaction on Cu(100) surface as sequential conversions of the C_2H_2 molecule into CCH and CC, on the basis of the results of their IETS analysis. Therefore, we performed IETS measurement to clarify whether the same process was occurring in our case, and show the results in Fig. 5(d). The intensity of the C-H stretch vibrational mode is greatly reduced by the reduction, indicating H desorption from the molecule. We concluded that the reaction that occurred here was the desorption of H atoms from the C_2H_2 molecule.

In conclusion despite its importance, tunneling spectroscopy and manipulation of adsorbates on the Cu(111) surface have not been analyzed in detail due to the strong influence of the standing wave on the spectra. We have shown that the inelastic tunneling spectra of a single C_2H_2 molecule adsorbed on a Cu(111) surface can be obtained clearly near the step edge, where the influence of the standing wave is reduced. The intensity of the C-H stretch mode on the spectra was comparable to that on Cu(100) surfaces, resulting in satisfactory manipulation and analysis of a single C_2H_2 molecule on the Cu(111) surface.

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*Present address: Tohoku University.

[†]<http://dora.ims.tsukuba.ac.jp>

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