

Adsorbate site determination with the scanning tunneling microscope: C₂H₄ on Cu{110}

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Scanning tunneling microscopy at $T=4$ K has been used to determine directly the binding site of a molecule chemisorbed on a metal surface, namely, ethene on Cu{110}, by simultaneous imaging of the adsorbate and the underlying lattice. The molecule is found to bond in the short bridge site on the close-packed rows with its C-C axis oriented in the $\langle 110 \rangle$ direction. [S0163-1829(96)05240-X]

The scanning tunnelling microscope (STM) offers a potentially powerful method of obtaining structural information on adsorbed atoms and molecules: If it is possible to image both the adsorbate and the corrugation of the substrate, then the adsorption site can be determined. In the past such investigations have been hampered by the high mobility of many adsorbed species on metal surfaces, even at 77 K. On the assumption that the activation barrier for surface diffusion is often below 100 meV,^{1,2} the mean residence time of the adparticle at 77 K is below 10^{-7} s, compared to a typical STM imaging time of the order of seconds. Eigler and co-workers³⁻⁵ have shown, however, that it is possible with a 4-K STM to image isolated adsorbed species. In high-coverage molecular adlayers, where diffusion is inhibited, imaging also becomes possible at noncryogenic temperatures, as shown in several recent papers, e.g., Refs. 6-13. For atomic adsorbates the interaction with the surface is often so strong that the imaging of isolated species may even be possible at room temperature.¹⁴⁻¹⁸ Defining the registry relative to the substrate is, however, still a problem because it is necessary to image both the adsorbate and the underlying lattice under the same conditions. The underlying lattice has been resolved mostly in the past by the technique of "corrugation enhancement" in which an adsorbate atom, or cluster of atoms, is brought (sometimes inadvertently) onto the apex of the tip.¹⁹ This leads, however, to a strong interaction between tip and substrate and thus to image distortion effects, which are poorly understood. A further possibility of determining the registry is to co-adsorb with another species of known adsorption site.^{10-12,20} This indirect method has the disadvantage that the influence of the coadsorbate on the adsorption process is generally not known. In the case of direct site determination of an isolated adsorbed molecule with a clean-tip high sensitivity and a wide dynamic range are required: Whereas the change in the z profile due to an adsorbate during constant current operation may be as much as 1-2 Å, the corrugation associated with a close-packed metal surface is of the order of 0.001-0.01 Å.

In the present paper we show how it is possible with a 4-K STM to image a small isolated adsorbed molecule with a clean tip and to determine directly its adsorption site. This has so far only been performed for a larger molecule, namely, benzene on Pd{110} with a somewhat stronger tip-to-sample interaction.²¹ Specifically, we have directed our attention to the adsorption site of ethene (C₂H₄) on Cu{110}. In a recent photoelectron diffraction (PD) study of this

system²² it was not possible to decide whether the molecule adsorbs in the short bridge site or in the atop site on the close-packed rows. We show here that the bridge site is occupied and, in agreement with the PD result, that the C-C axis is oriented in the $\langle 110 \rangle$ direction. Quantitative techniques such as low-energy electron diffraction (LEED) and PD, which "average" structurally over the surface are of course also available, not only for the determination of adsorption site and molecular orientation, but also of bond distances and angles. STM, on the other hand, has the potential advantage of providing rapidly and directly structural information on a molecular level, even if it is quantitatively more limited in scope.

The measurements were performed with a low-temperature STM similar to the one developed by Eigler.²³ High stability is characteristic of the design in which the ultrahigh vacuum (UHV) chamber of the microscope is completely cooled and effectively decoupled from external vibrations by a pendulumlike suspension with very low resonance frequency (0.6 Hz). Helium gas provides thermal coupling as well as acoustic insulation between the dewar and the STM flange. By varying the He pressure in the exchange gas chamber and by changing the coolant in the dewar from helium to nitrogen the temperature of the STM can be set between 4 and 300 K. A fundamental difference to Eigler's design is a purely mechanical coarse approach based on a lever system which offers the possibility of conducting experiments at different temperatures. The Cu{110} single crystal was prepared by standard polishing techniques as well as by *in situ* Ar⁺ sputtering and annealing cycles in order to obtain clean, atomically flat, 500-Å-wide terraces as monitored by STM. High coverage ethene layers were prepared by dosing $<1 \times 10^{-6}$ mbar s of the gas to the sample at $T=120$ K. The sample was then transferred from the upper UHV chamber with a base pressure $<5 \times 10^{-11}$ mbar down to the STM chamber where, because of the very good vacuum conditions at 4 K, the sample surface remains unchanged over a period of days. Low coverage images were obtained by adsorbing at 4 K in the microscope itself.

For the STM investigations a Pt/Ir tip was cleaned and sharpened in the microscope. In a first coarse treatment a voltage of 300 V was applied and the tip moved toward the surface until the field emission current reached 1 μ A. Depending on the polarity the tip was then further prepared with field emission until the current stabilized²⁴ or by field desorption until the end of the tip tore away and the current broke down.¹⁹ In a second step after the approach of the tip

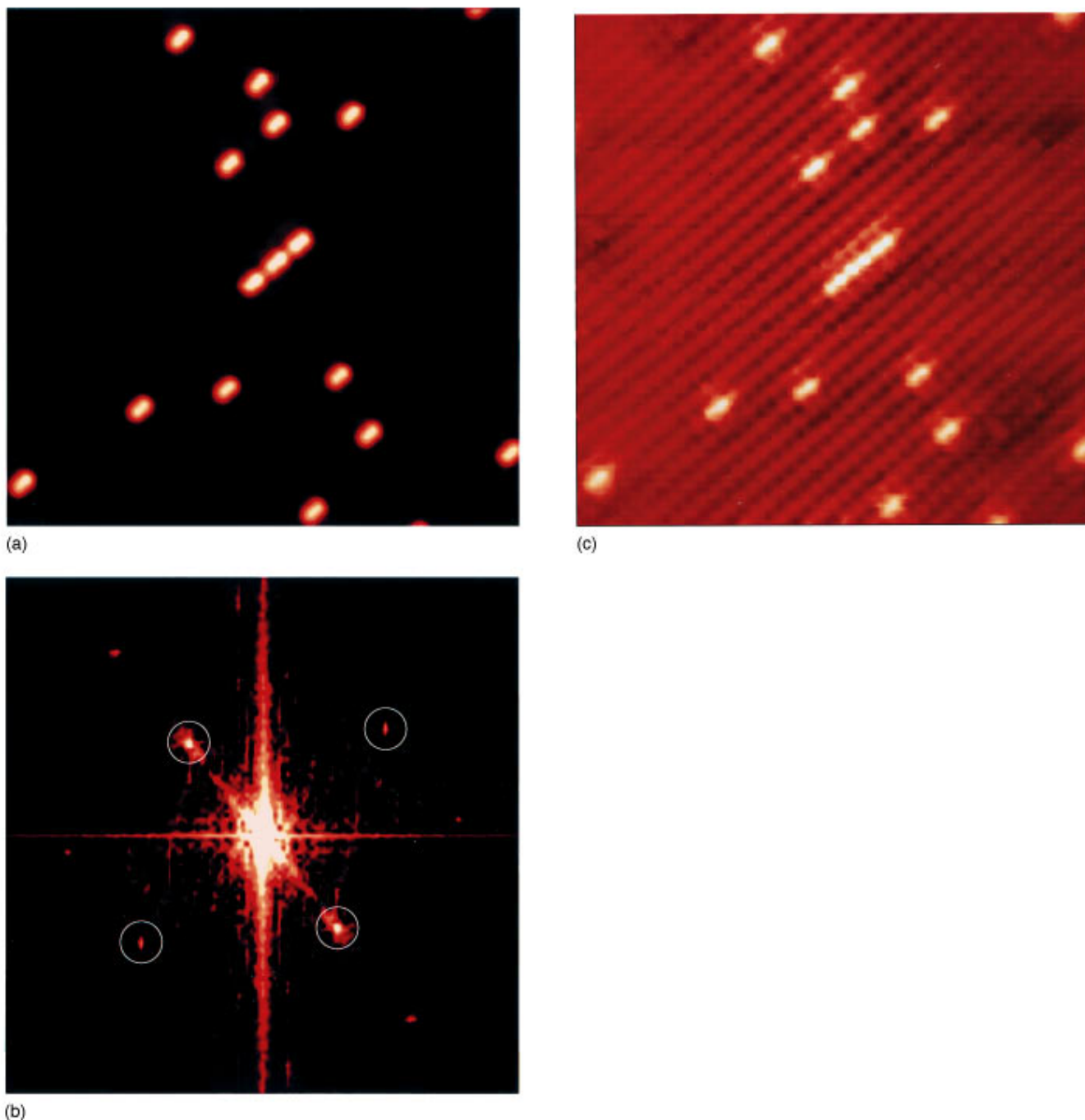
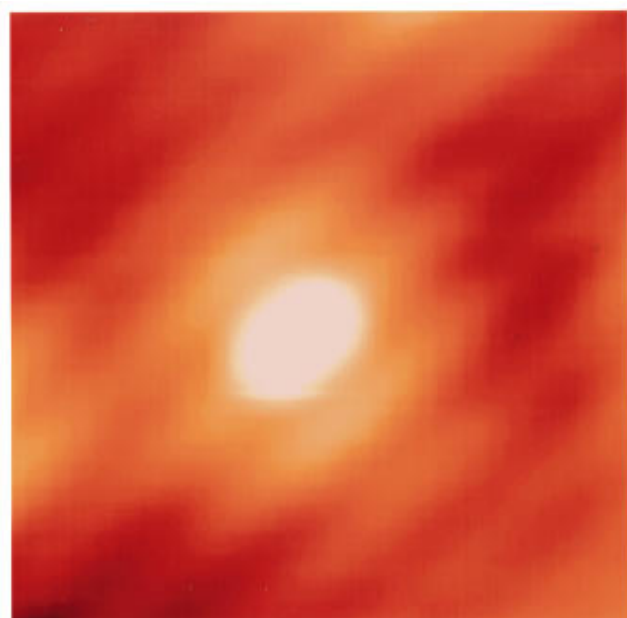


FIG. 1. STM images of a 0.03-ML ethene layer adsorbed on a Cu{110} surface ($80 \times 80 \text{ \AA}$): (a) Unprocessed data. 500 pA; 20 mV. (b) Fourier transform of the image (a). (c) The back-transform of the main features as ringed in (b), i.e., the filtered image, with 30% of the original image (a) superimposed. Note that the relative dimensions of the {110} unit cell are not reproduced because the piezos are not exactly orthogonal.

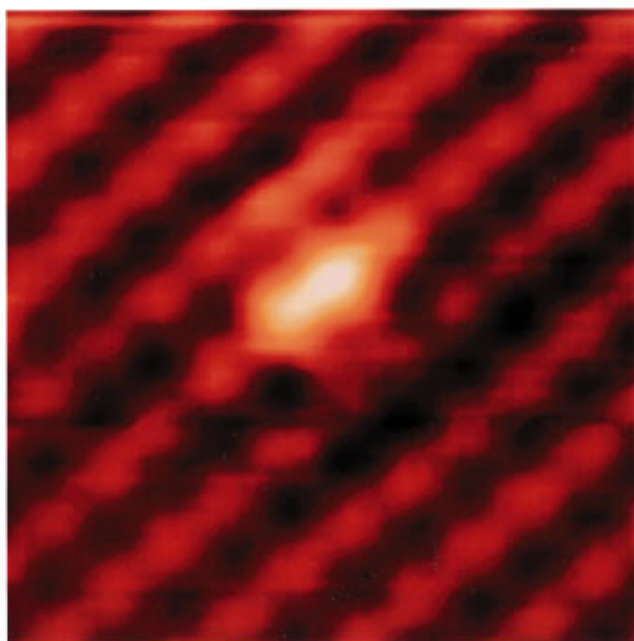
into the tunneling range, clusters of atoms or molecules can be transferred at positive sample bias from the tip to the sample and at negative sample bias in the reverse direction. The number of transferred atoms depends on the magnitude of the voltage (1–10 V).

In the present work emphasis was placed on preparing a clean tip, rather than an adsorbate-covered tip, so as to minimize the interaction with the surface and thus the distortion of the image. This means that the magnitude of the metal surface corrugation is at least two orders of magnitude lower

than that which can be achieved by imaging with atoms or clusters which have been picked up by the tip.¹⁹ This is immediately apparent in Fig. 1(a) which shows a constant current image (field of view $80 \times 80 \text{ \AA}$) of an approximately 0.03 ML ethene layer chemisorbed on Cu{110}. The bright features, not present on an unexposed surface, are superimposed on a very weak, striped structure (not visible in the figure) which we identify as the close-packed rows parallel to the $\langle 110 \rangle$ direction. The striped structure only becomes visible when the gray-scale distribution is restricted to a few



(a)



(b)

FIG. 2. An individual ethene molecule ($23 \times 23 \text{ \AA}$) from (a) the unprocessed image [Fig. 1(a)] (b) the processed image [Fig. 1(c)].

tenths of an \AA , as in Fig. 2(a). The single adsorbate-related feature in this expanded-view image is then out of range and appears as an “overexposed,” structureless spot. All the adsorbate-related features are slightly elongated in the $\langle 110 \rangle$ direction and centered over the close-packed rows. This result confirms the earlier photoelectron diffraction study in which the adsorption site of the ethene molecule was found to be on the close-packed rows with the C-C axis oriented approximately in the $\langle 110 \rangle$ crystal azimuth.²² Note that in the center of the image in Fig. 1(a) three ethene molecules are adsorbed on adjacent sites. This is the result of inadvertent manipulation of molecules with the STM tip. In fact, we have been able to move ethene molecules by field

manipulation^{25,26} to form such molecular chains. In the following we describe how the adsorption site on the rows has been determined.

To distinguish between the top and short bridge sites it is necessary to enhance the lattice corrugation. Figure 1(b) shows the Fourier transform of the image which is the log (power spectrum) of Fig. 1(a). A reverse Fourier transform of only those regions around the “integral order features” defined by the rings in Fig. 1(b) was then performed (the rings are not sharp cutoff functions, but have a Gaussian profile.) This simple technique for enhancing the resolution of STM images appears to have first been used by Park and Quate.²⁷ By now superimposing 30% of the intensity of Fig. 1(a) onto the reverse transformed image we obtain the image of Fig. 1(c). The latter not only reveals the discrete structure of the Cu atoms along the $\langle 110 \rangle$ rows but also shows that all the molecules occupy the short bridge site rather than the atop site. This was found to be the case for all the images studied. Figure 2(b) shows an enlarged view of one of the molecules from Fig. 1(c). The photoelectron diffraction investigation²² was unable to distinguish between the two adsorption sites because of an ambiguity related to the fact that the C-C bond length is approximately half the Cu interatomic separation. The occupation of the short bridge site is an interesting result in that the vibrational spectrum of C_2H_4 on this surface²⁸ corresponds to that of type II in the classification scheme of Sheppard.²⁹ Molecules of this sort are characterized by a symmetric C-H stretching vibration in the range $2990\text{--}3075 \text{ cm}^{-1}$ and a C-C stretch of the deuterated species in the range $1320\text{--}1420 \text{ cm}^{-1}$, implying a bond order of about 1.7. In the past such spectra have been taken as indicative of a so-called π -bonded species which might be expected to occupy an atop site, at least by comparison to certain compounds in organometallic chemistry, where a similar bonding configuration occurs.

By approaching the manipulation regime of Eigler and Schweizer³⁰ (corresponding to a tunnel gap impedance of $10^6 \Omega$) it is possible to rotate the ethene molecules out of the $\langle 110 \rangle$ direction by about 20° . We note that this value is the same as the (unexpectedly large) uncertainty in the determination of the azimuthal orientation with photoelectron diffraction.²² At high coverages, corresponding to the conditions under which the photoelectron diffraction experiments were performed, several molecules in a $100 \times 100 \text{ \AA}$ image were found which spontaneously took up this configuration. Otherwise, the images of all the other molecules appeared to be identical with those at low coverage.

The image of the adsorbate in Fig. 2(b), while clearly showing the registry of the adsorbate relative to the substrate, is subject to some distortion in that the positions of the two maxima associated with the adsorbate have a larger separation than those in the unprocessed image. A section through an ethene molecule in the $\langle 110 \rangle$ direction (i.e., along the close-packed row) from the unprocessed image of Fig. 1(a) is shown in Fig. 3. In the processed image the two maxima are coincident with those of the Cu lattice, which is due to the fact that only the frequencies associated with the latter are selected in the filtering process. The two maxima in the raw image are separated by approximately 1.4 \AA which compares to the C-C bond length in the free C_2H_4 molecule

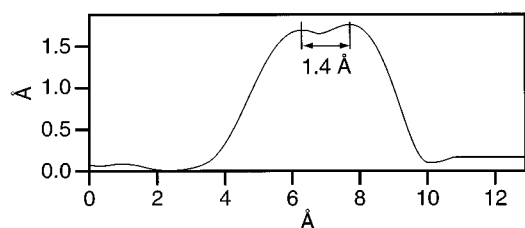


FIG. 3. Section through a single ethene molecule along a line in the $\langle 110 \rangle$ direction (unprocessed data).

1.32 Å and to the C-C bond length in the photoelectron diffraction result for the short bridge site of $1.53 (\pm 0.13)$ Å.²²

In the case of molecules, polymers and bio-organic materials it is generally accepted that the STM does not give the location of the atomic cores. Rather, it is sensitive to variations in the electron density on the atomic scale. Ohtani *et al.*⁶ were the first to record an apparent internal structure associated with an adsorbed molecule, namely, for benzene in a close-packed co-adsorbed layer with CO. In a more recent study by Weiss and Eigler⁵ three distinct types of image for an isolated benzene molecule on Pt{111} were obtained and assigned to different surface sites. This agrees with calculations for this system by Sautet and Bocquet³⁰ who showed that threefold hollow and bridge sites should indeed give benzene images indicative of C_{3v} and C_{2v} symmetry, respectively. One can rationalize the influence of the surface site by noting that the bonding interaction between substrate

and adsorbate orbitals can give rise to changes in electron density in the region of the Fermi level. (It should perhaps be mentioned that for the present system there is no systematic photoemission or inverse photoemission study of this effect in the literature.) Returning to a previous paper of the Eigler group⁴ we note further that the shape of the image of isolated CO molecules on the same surface (“sombbrero” or “protrusion”) is also strongly dependent on the position of the molecule on the surface. The implication is again that the surface sites, in this case atop and bridge, affect the shape of the molecule in the STM image. It is therefore not unreasonable to assume that the twofold symmetry of the short bridge site in the present case of ethene plays an important role in the observation of the two maxima in Fig. 3, even if the separation of the maxima is ~ 1.4 Å compared to the Cu nearest-neighbor distance of 2.56 Å.

In conclusion, we have shown that it is possible with a low temperature STM to determine the adsorption site and azimuthal orientation of an isolated adsorbed hydrocarbon molecule on a metal surface. This involves imaging the adsorbate with a weak tip-to-sample interaction at the same time as resolving the substrate corrugation. The molecule in question, ethene (C_2H_4), adsorbs in the short bridge site on the close-packed rows with its C-C axis oriented in the $\langle 110 \rangle$ direction. Future application of the technique to other adsorbates at low temperature is foreseen.

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