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# Acetylene structure and dynamics on Pd(111)

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Acetylene molecules adsorbed onto a Pd(111) crystal surface were imaged by scanning tunneling microscopy (STM) below 70 K. Single $C_2H_2$ molecules appeared as a combination of a protrusion and a depression 3.5 Å apart. This peculiar shape is due to the molecular $\pi$ orbital, which is oriented at a shallow angle out of the surface. Six orientations of the molecule with respect to the substrate were observed, indicating two different threefold hollow binding sites each with three possible rotational states. At 44 K, thermally activated rotation of the molecules between the three equivalent states on the same threefold hollow site occurs on the time scale of seconds. Diffusion of molecules between adjacent threefold sites began at ~70 K. The findings agree with the structure of the adsorption site determined by total-energy calculations and with the STM image calculated using the electron scattering quantum chemistry method. [S0163-1829(98)50320-7]

Atomic resolution imaging of atoms and molecules on catalyst surfaces to determine their structure and to follow their reaction pathways is one goal of surface science. Variable temperature scanning tunneling microscopy (STM) has the potential to accomplish this goal by providing a direct view of the structure and dynamics of the molecular adsorbates. In principle, the rate of each step in the reaction can be brought into the time scale of STM imaging (seconds to minutes) by adjusting the temperature of the surface. In addition, atomic manipulation of reactants with the tip opens the possibility of inducing and exploring specific reactions pathways. In our laboratory, we are performing these studies with the catalytic reaction of acetylene cyclotrimerization to form benzene on Pd(111). Here we present results that show in unprecedented detail the structure of the adsorbed acetylene molecule and its conformational changes as it moves over the surface of Pd(111).

A considerable amount of information on this reaction has emerged from studies performed over the past 15 years.[1–3] The reaction occurs under both high pressure on dispersed catalysts[4] and on single crystals in ultrahigh vacuum (UHV). It is highly structure sensitive and selective on the Pd(111) surface, with up to 35% of the acetylene converted to benzene in UHV. Low-energy electron diffraction studies indicate that acetylene orders in a $(\sqrt{3}\times\sqrt{3})R30°$ lattice.[5,6] Kesmodel *et al.* have acquired vibrational spectra that indicate that the molecule is rehybridized upon adsorption to approximately $sp^{2.5}$.[7,8] They proposed a model in which the molecule is associated with three metal atoms and lies with its C-C bond parallel to the surface.[8] Photoelectron spectroscopy studies[6] indicate that the $\pi$ orbital degeneracy is broken by the adsorption symmetry. Sellers[9] performed theoretical calculations of the molecule on clusters at high-symmetry binding sites. The results fit best with the vibrational spectrum for the molecule bound at a threefold hollow site with a C-C bond length of 1.41 Å, a C-H length of 1.09 Å, and a C-C-H angle of 129°. The molecular plane was tilted 22° from the surface normal. Lambert *et al.*[10] have compared near-edge x-ray-absorption fine-structure spectra with calculated spectra for acetylene adsorbed at various sites using the geometry derived from Sellers' calculations. The best agreement was found for the threefold hollow site geometry with the C-C bond parallel to the surface. All these studies, however, were performed at temperatures above 90 K. As we shall see, individual molecules are already rotating very fast at these temperatures. In order to form a better understanding of the $C_2H_2$ adsorption, dynamics and the starting point of this reaction, we imaged single molecules of $C_2H_2$ adsorbed at low coverage on the Pd surface at temperatures from below those at which diffusion or reaction takes place through the onset of thermal diffusion and reaction.

The experiments were performed in an UHV chamber with a base pressure of $2\times10^{-10}$ Torr incorporating standard surface science instruments, and a variable temperature inverted beetle-type STM. The Pd(111) sample was mounted onto a vibration damped stage at the end of a combination manipulator/cryostat cooled by liquid He.[11] The crystal was cleaned by repeated cycles of sputtering with 700 eV $Ar^+$ at 3 $\mu$A while heating to 1200 K to remove S. It was heated to 800 K in $10^{-7}$ Torr of $O_2$ to remove carbon. After cleaning, the sample was cooled to 35 K over approximately 1 h. Acetylene gas was introduced through a leak valve to dose the crystal to the desired coverage, typically a few percent of a monolayer, as measured by counting the number of molecules per unit area in the STM images. Chemically etched Pt/Rh 10% alloy wires were used for the tips. They were cleaned by field emission in vacuum. The cleanliness of the tip was verified by measuring the rate of tunneling current decay with tunneling gap distance, which is one order of magnitude per Å for a clean tip. Images were acquired in topographic (constant current) mode at a scanning rate of 0.5–2 $\mu$m/s.

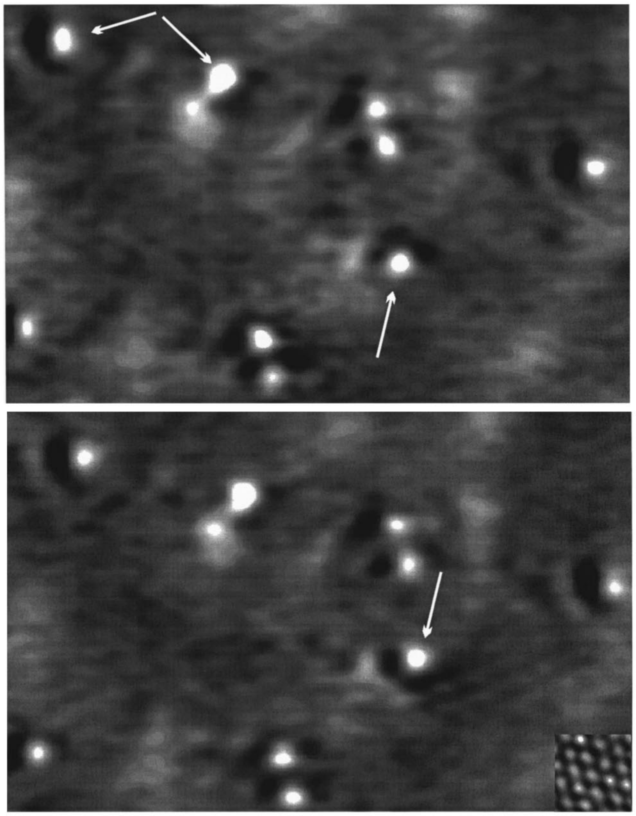

FIG. 1. Two 78×50 Å images (15 mV, 116 pA, 129 MΩ) of the surface from a sequence at 44 K after exposure to $C_2H_2$. An atomic resolution image of the clean Pd surface taken several minutes earlier is shown at the same scale in the inset. Acetylene molecules appear as a protrusion with a shallower adjacent depression. The three arrows in the upper frame show the possible molecular orientations at one type of a threefold site. The arrow in the lower frame indicates a molecule that has diffused to the other type of a threefold site, for example, from hcp to fcc hollow.

Figure 1 shows two frames from a sequence of STM images of the surface obtained at a temperature of 44 K after dosing with $C_2H_2$. Nine molecules are visible in this area of 600 Pd atoms. Each molecule appears as a combination of a protrusion with a shallower depression located several Å s away. The total corrugation of the molecule is ~0.2 Å at a tunneling gap resistance of 100 MΩ and increased by ~50 % when the gap is reduced to 10 MΩ. While the height and size of the protrusion remain nearly constant with tunneling and tip conditions, the depth of the depression varied. The inset in Fig. 1 shows a small part of an atomically resolved Pd image at the same scale that was obtained nearby at a gap resistance of ~100 kΩ. The tip sweeps away the acetylene molecules at the low gap resistance required to resolve the Pd(111) lattice.

The molecular protrusion-depression combination appears in six different orientations separated by 60°. The arrows in the upper frame of Fig. 1 indicate three molecules whose orientations differ by 120°. A close-up image of a molecular feature with a cross section through the protrusion and depression is shown in the left-hand side of Fig. 2. This line is perpendicular to the compact rows of atoms on the Pd(111) surface. At 44 K and above, the orientation of any specific $C_2H_2$ molecule could be observed to switch randomly between three rotational states. Rotation was sometimes observed within an image, resulting in a discontinuity in the molecular feature. To follow the dynamics more closely, several sequences of ~100 images each were taken at the same location at a rate of 10 sec per image. These images were played back quickly in the form of an animated movie. The protrusions associated with each molecule usually remained confined to a single site, but changed in orientation at random intervals about this site in a triangular pattern. A sample movie is available in mpeg format on our Web site.[12] These results clearly indicate that acetylene bonds in both the hcp and fcc threefold hollow sites, with each site having three different angular orientations. The observed orientations for molecules adsorbed at hcp sites will be rotated 60° relative to the observed orientations at fcc sites. One molecule that has diffused from one type of site to the other is indicated by the arrow in the lower frame of Fig. 1.

Although the molecules are able to rotate among three equivalent orientations at each site at 44 K, diffusion to adjacent sites is much slower. The rate at which the molecule jumps between rotational orientations increases with temperature and can also be influenced by the presence of the tip. The details of the tip-molecule interaction are under investigation and will be reported separately. When the tip influence is minimized, an energy barrier for a rotation of 113 meV can be estimated (±10%), using a preexponential factor of $10^{13}$ Hz. Diffusion of the isolated molecules between different threefold hollow sites is observed at ~1 per 100 sec at 65 K and reaches ~1 per second at 70 K. This indicates an activation energy on the order of 180 meV.

To better interpret these results, total-energy calculations were performed to determine the most stable site of the acetylene molecules. We used a density-functional theory with the generalized gradient approximation, implemented using the Vienna *ab initio* simulation program.[13–15] Details of the calculation will be reported later. Adsorption at hollow sites was strongly favored, with the hcp site being slightly lower in energy (by 15 meV) than the fcc site. In the lowest energy geometry, the molecule adopts a bent configuration with a C-C-H bond angle of 129°. The molecule is offset slightly from the center of the threefold site and tilted by ~13° from the surface normal away from the Pd-Pd pair parallel to the C-C bond. These results, similar to those of Sellers cluster calculations,[9] are shown schematically in Fig. 3.

In either hollow site, the adsorption energy with the C-C bond oriented parallel to the Pd-Pd bond was significantly lower than that for the perpendicular orientation (145 meV for hcp, 136 meV for fcc, see Fig. 3). These values are not too far from the experimentally estimated value of 113 meV for the energy barrier for single-site rotation. For the site with the C-C bond parallel and directly above the Pd-Pd bridge site, the most favorable bridge geometry, the calculated energy is 360 meV, which is a factor of 2 larger than the estimated translation activation energy of 180 meV.

The ESQC method[16,17] was then used to calculate the STM acetylene images, starting from the most stable geometry. The result is shown on the right-hand side of Fig. 2 as a topographic map of the surface at constant tunneling conductance overlaid on a schematic of the adsorbed molecule.

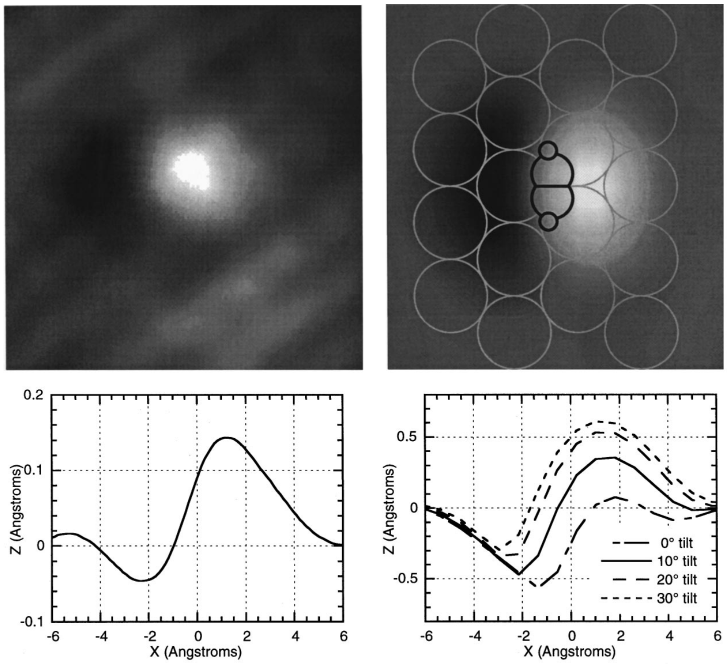

FIG. 2. Left: A 12×13 Å image of an acetylene molecule (40 mV, 400 pA, 100 MΩ). The graph below shows a cross section along a path through the maximum and minimum of the image. The maximum is 0.13 Å high, the minimum 0.07 Å deep, and they are separated by 3.5 Å. Right: A 12×13 Å ESQC calculated STM image for the minimum energy geometry. As in the experiment, the molecule appears as a protrusion next to a depression, neither of which is at the position of the molecule itself. The calculated image is overlaid on a schematic of the adsorbed molecule. The graph shows the calculated molecular profile vs molecular tilt angle off normal. As the tilt angle increases, the protrusion increases as the depression decreases. As explained in the text, this is the result of changes in the $\pi$ orbital overlap with the tip.

The simulated image consists of a protrusion and a depression, in good agreement with the experiment. The protrusion associated with the molecule is located close to the bridge site adjacent to the adsorption site. Rotation of the molecule at the single threefold site shifts the position of this protrusion between the three adjacent bridge sites, also in agreement with the observed dynamics. The predicted corrugation of the molecule was several times larger than that found experimentally. This could be due to approximations made in the ESQC calculation or to a discrepancy between the actual unknown tip termination and the ideal single Pd atom-terminated tip used in the calculation. Details of the calculations will also be reported separately.

Figure 2, right-hand side, shows calculated cross sections through the molecule as a function of the molecular tilt angle. The calculated image for an untitled molecule has a depression slightly offset from the hollow site with a much smaller protrusion on the other side. As the molecule tilts, the relative size of the protrusion increases as the depression decreases and shifts away from the molecule. At the tilt angle predicted by the total-energy calculation (13°), the image shape is in good agreement with the experiment. The observed image shape can be explained qualitatively in a simple way. The acetylene $\pi$ orbital was found to have the largest overlap with the tip orbitals. This antisymmetric orbital is oriented perpendicular to the plane of the molecule. If the molecular plane was normal to the surface, the positive and negative lobes of the $\pi$ orbital would extend out on each side of the molecule and their overlap with the tip $s$ orbital would interfere and cancel out. Because of the 13° tilt of the molecule, the overlap with one lobe makes a dominant con-

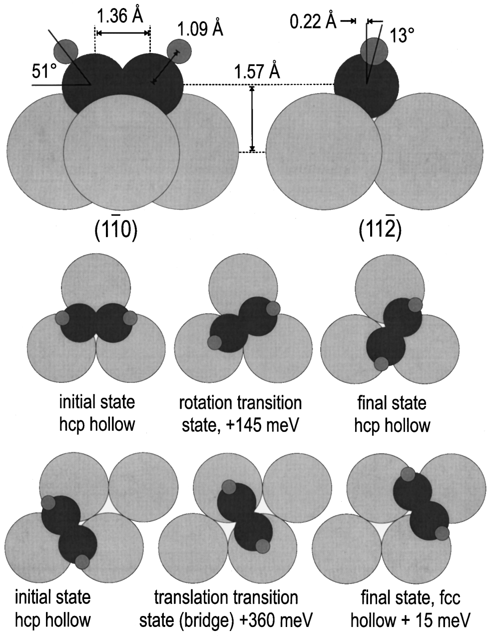

FIG. 3. Top: Geometry of the adsorption site of acetylene on the Pd(111) surface obtained from total-energy calculations, as explained in the text. The lowest energy corresponds to the hcp hollow site, followed by the fcc site, which is 15 meV higher. The molecule is offset from the center of the threefold hollow site by 0.22 Å away from the Pd bridge site parallel to the C-C bond. The molecular plane is also tilted 13° away from the bridge. Center: Schematic diagram of molecular rotation showing the transition state and the theoretical energy barrier. Bottom: A similar diagram showing the transition state for diffusion between hollow sites.

tribution to the image, and the protrusion associated with the molecule is off center. The depression in the image is a result of the interference between the surface and molecular contributions.

In conclusion, by combining cryogenic STM imaging experiments and calculations, the adsorption geometry and dynamic behavior of $C_2H_2$ on the Pd(111) surface have been determined in considerable detail. Acetylene binds at both hcp and fcc threefold hollow sites, with the C-C bond parallel to the surface and aligned with the compact rows of Pd atoms. The plane of the molecule is tilted slightly off normal (13°). Due to this tilt, the molecular $\pi$ orbital has a strong overlap with the STM tip on one side, producing a protrusion in the image on one side of the molecule. The molecule is observed to rotate on one site among three orientations on a time scale of seconds at 44 K, but does not diffuse readily between sites until almost 70 K.

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