When Scanning Tunneling Microscopy Gets the Wrong Adsorption Site: H on Rh(100)

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At low tunneling resistance, scanning tunneling microscopy (STM) images of a Rh(100) surface with adsorbed hydrogen reproducibly show protrusions in all bridge sites of the surface, leading to a naive interpretation of all bridge sites being occupied with H atoms. Using quantitative low-energy electron diffraction and temperature programmed desorption we find a much lower H coverage, with most H atoms in fourfold hollow sites. Density functional theory calculations show that the STM result is due to the influence of the tip, attracting the mobile H atoms into bridge sites. This demonstrates that STM images of highly mobile adsorbates can be strongly misleading and underlines the importance of additional analysis techniques.

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Within the two decades since its invention, scanning tunneling microscopy (STM) has led to a revolution in studies of solid surfaces. As STM delivers real-space images, which appeal to our visual sense and are often straightforward to understand, one usually takes these images as bona fide representations of the surface structure. Physicists have gotten accustomed to the main limitation of a simple interpretation, i.e., the fact that STM maps the electronic structure of the surface, not the true geometric structure, so some adsorbates sitting on the surface may be imaged as depressions [1,2]. When taking this into account, determination of the adsorption sites, symmetry, or the coverage is considered unproblematic. It is well known that interaction of the STM tip with atoms or molecules on the surface can lead to an enhancement of corrugation amplitudes [3], to chemical contrast between elements of an alloy [4] and to artifacts in measurements of the dynamics on a surface, e.g., diffusion measurements [5], but more qualitative studies such as determination of a structure are not considered prone to such problems. In the current work, we will demonstrate that ignoring tip-sample interaction can lead to severe misinterpretation of STM images with regard to structure, symmetry, and adsorbate coverage.

The adsorbate/surface system chosen for our study is hydrogen on Rh(100). The adsorption of hydrogen on transition metals has been extensively studied, mostly with respect to fundamental catalytic reactions and energy storage possibilities. Hydrogen on Rh(100), in particular, is a prototype system for H adsorption and is remarkable because of the low difference of adsorption energy between adsorption in hollow and bridge sites of less than 0.1 eV. Nevertheless, all *ab initio* calculations agree that H favors adsorption in hollow sites [6], but also in bridge sites a local minimum of the energy is found. Whereas the unsatisfactory agreement between calculated [6] and experimental [7] relaxations might shed some doubts on this result, an extensive high-resolution electron energy loss spectroscopy study of H on Rh(100) [8] has also shown that H is situated in hollow sites at 90 K, at coverages up to one monolayer (ML). As all these results are valid for low temperatures only, and in view of the small energy difference between hollow and bridge sites, these results do not necessarily yield the correct room-temperature adsorption site.

However, a direct detection of hydrogen has always posed a difficult task in surface science, and it is usually not seen on metals by STM at all. Even on metal surfaces where an H-induced reconstruction is observed, attempts to directly image the adsorbed hydrogen atoms were not successful [9,10], the only possible effect being a slight elongation of the protrusions caused by the metal atoms. In the case of hydrogen on Cu(100), clear images of H atoms at low temperature were reported [11], but in contrast to our findings they always appeared as depressions.

The STM and LEED measurements were done in Vienna in two separate UHV chambers with base pressures better than 5×10^{-11} mbar. The hydrogen partial pressure in the LEED chamber was below $1 \times$ 10^{-11} mbar as determined by a quadrupole mass spectrometer. The STM images were taken at room temperature by a customized Omicron micro-STM with an electrochemically etched W tip in constant current mode with the sample at negative voltage. The LEED measurements were performed at normal incidence of the primary electron beam using a two grid system and video data acquisition. For the LEED calculations the TensErLEED program package [12] was used, where an energy dependent inner potential [13] was implemented. The hydrogen coverage was varied using the average t matrix approximation [14]. To determine the agreement between measured and calculated I-V curves the Pendry R factor [15] was chosen. Quantitative temperature programmed desorption (TPD) measurements were done in Graz, where the UHV chamber was additionally equipped with a calibrated desorption standard which allowed absolute coverage determination [16]. Prior to our experimental study the crystals were cleaned by several Ar^+ sputtering-annealing cycles, followed by a final annealing step at 750 °C. According to Auger electron spectroscopy, the samples were then free from C, O, and S contaminations.

The calculations were performed using the plane wave based density functional code VASP (Vienna ab initio simulation package) [17] employing the projector augmented wave method [18,19] ($E_{cut} = 250 \text{ eV}$). For exchange and correlation generalized gradient corrections according to Perdew et al. [20] have been applied. The surface was modeled by seven- and eight-layer slabs with periodic boundary conditions (with the geometry of the uppermost three metal layers and the H layer optimized), sampled in reciprocal space by a grid of $(11 \times$ 11) k points. The topography of the bottom surface of the slab was designed to represent an STM tip by placing one single Rh atom in the center of a (2×2) cell, protruding from the surface. Also at this side of the slab the coordinates of the tip and the underlying layer were optimized. Subsequent slabs are separated in the z direction by a vacuum varied between 14 and 3 Å, so that the approach of the bottom surface of the repeated image (for small vacuum width) mimics the influence of the STM tip. For an accurate description of the site preference the inclusion of zero-point energies is crucial (100 meV for hollow, 167 meV for bridge sites) due to the small adsorption energy differences for Rh(100).

Room-temperature STM images of both the pure Rh(100) surface as well as those of various PtRh(100) alloy surfaces exhibit regular corrugation; i.e., the metal atoms appear as protrusions under all tunneling conditions where the atomic corrugation is visible at all, down to very small tip-sample distances (tunneling resistance $R_T < 100 \text{ k}\Omega$). This situation changes already after adsorption of a rather small amount [4-15 L (Langmuir, where $1 L = 10^{-6}$ Torr s); values given in this Letter are corrected for the sensitivity of the ion gauge] of molecular hydrogen. Whereas we find regular corrugation at medium R_T (> 100 k Ω), at low tunneling resistance the bridge sites appear as maxima in the STM images (Fig. 1). The occurrence of bridge-site maxima at low R_T is reproducible on both pure Rh(100) and on PtRh(100)surfaces with a high surface concentration of Rh. The transition from regular to bridge-site corrugation is smooth and reversible. Only the exact value of the tunneling resistance where the transition occurs depends somewhat on the state of the tip. These observations indicate that we see a genuine surface property, and it is therefore tempting to attribute the bridge-site maxima to hydrogen. Taking the STM images at face value, an occupation of all bridge sites by H would correspond to an H coverage of 2 ML, a value unusually high for room temperature.

To determine the true adsorption site of H on Rh(100) we performed a quantitative LEED study of the hydrogen



FIG. 1. Room-temperature STM images $(50 \times 50 \text{ Å}^2)$ of the same area of a Rh(100) surface after exposure to 15 L of H₂ at (a) 0.5 mV, 4 nA ($R_T = 125 \text{ k}\Omega$) and (b) 0.5 mV, 9 nA ($R_T = 55.6 \text{ k}\Omega$). Using the various defects and impurities as markers, one can easily determine that the protrusions in (b) are in bridge sites.

saturated Rh(100) surface at various temperatures, as well as quantitative TPD. Since hydrogen is a very weak scatterer for electrons, various cross-checks, regarding the sensitivity of LEED towards hydrogen, were performed. For the clean surface a calculation with variable H-coverage resulted in the true coverage of 0%. For the H-saturated surface calculations without the consideration of the presence of hydrogen result in poor agreement with the experiment, with an R factor significantly above the error bars determined by LEED (see Fig. 2). Hence, due to these results and the good agreement between calculation and experiment we are sure to be able to determine the H coverage in bridge and hollow sites with reasonable accuracy. As a by-product of our investigations we are now able to close the gap between experimental and theoretical results concerning the relaxation of the first interlayer distance of a clean Rh(100) single crystal [7], in favor of an inward relaxation (1.57% at room temperature), which is increasing as the temperature is reduced.



FIG. 2. LEED results for a hydrogen covered Rh(100) surface at 5×10^{-8} mbar H₂ background pressure and room temperature (Pendrys *R* factor for various models on the *x* axis). The grey bar indicates the range of models compatible with the LEED data.

For the quantitative LEED analysis three different models were considered: Hydrogen adsorption in bridge or hollow sites only and a mixture of both possible adsorption sites. The total energy range available for this analysis was 1800 eV (using seven symmetryinequivalent beam sets) and up to 12 parameters were varied. At low temperatures (120 K), after dosing 60 L of molecular hydrogen, we find a hydrogen saturation coverage of 1.1 ± 0.6 ML [21], thereof 0.9 ML in hollow sites. For comparison, quantitative TPD yields a saturation coverage of 1.22 ML [22], which also shows that, in addition to H atoms being situated in hollow sites, bridge sites have to be occupied. At room temperature we find only very low coverages (too low for reliable quantification by LEED) in UHV after adsorption. Sizable amounts of adsorbed H are found at a background pressure of 5×10^{-8} mbar. In this case the models with hydrogen being situated in bridge or hollow sites only were ruled out, favoring the mixed model with a total H coverage also near 1.1 ML, but thereof roughly two thirds in hollow sites and one third in bridge sites (Fig. 2). Given the low energy difference mentioned above, we believe that this result differs from the low-temperature occupation due to thermal excitation of H atoms into bridge sites. Well-converged density functional theory (DFT) calculations for a coverage of 1 ML result in an energy difference of 87 meV between bridge and hollow sites (including zero-point energy corrections), also indicating that at least some of the bridge sites have to be occupied at room temperature. Adsorption isotherms which have been extracted from a series of thermal desorption spectra show the equilibrium coverage at 300 K and 5 \times 10^{-8} mbar to be about 1 ML, in reasonable agreement with the LEED result. On the other hand, the amount of H remaining on the surface after dosing 15 L at room temperature (the preparation used for the STM measurements) is very low (about 0.25 ML), which is in clear contradiction to an occupation of all bridge sites, as suggested by a naive interpretation of the STM images.

The solution to this puzzle comes from DFT calculations of the H-adsorption/potential energies [23] when the STM tip is approached towards the surface. We have used one hydrogen atom in a (2×2) cell to simulate a low H coverage (as present in the STM experiments). We define the hydrogen potential energy as the total energy difference per (2×2) cell between a configuration with and without adsorbed hydrogen, taking half of the energy of an H₂ molecule (including zero-point corrections) as reference energy for the H atom. Because of the force between tip and sample it is important to use the energies after relaxation. A lot of different scenarios were investigated with regard to the tip position above the surface and the various possible H-adsorption sites in the (2×2) cell [cf. Fig. 3(a)]. As a general trend, we find that the total energy decreases for all configurations where the hydrogen atom is located very close to the tip as it approaches the H-covered surface, whereas all other models get energetically more and more unfavorable [Fig. 3(b)]. In other words, the tip attracts the H atoms and thereby increases the local coverage at the site where it images the surface. We further find that the small difference between bridge and hollow site potential energies is reversed at small distances if the tip approaches the surface close to the position of the H atom. Because of the high surface mobility of hydrogen at room temperature (calculated diffusion barrier is $\approx 0.1 \text{ eV}$) these displacements happen at a much shorter time scale than the scanning speed. This fact and the increased local H coverage are the reasons why the tip always finds, at a sufficiently small tip-sample distance, the bridge site currently imaged occupied with an H atom. This view



FIG. 3. (a) Top view of (2×2) cells with different tip-hydrogen configurations considered by DFT. (b) Potential energies per H atom depending on the vacuum size (before relaxation) for all calculated models. Full symbols show the values for adsorption in hollow sites and open symbols in bridge sites; triangles depict results for seven-layer slab, circles for eightlayer slab.



FIG. 4 (color online). DOS plots at $E_F \pm 50 \text{ meV}$ of a Rh(100) surface with H in bridge sites. (a) Geometry with large vacuum; (b) geometry with small gap, showing a pronounced outward relaxation of the hydrogen and an increased DOS at the H positions for small tip-sample distances.

is further supported by the remarkably good agreement between calculation and experiment of the critical tipsample distance, where the bridge sites get energetically more favorable, both indicating ≈ 1 Å (3.8 Å core-core) as the critical gap width.

However, that still does not explain the extraordinary feature why one sees the hydrogen atoms with the STM, since density of states (DOS) plots at the Fermi level E_F of slabs with an unperturbed surface (i.e., a large vacuum) show no indication of that feature. In this case the H atoms should be invisible because the Rh atoms appear higher. At small tip-sample distances, however, the H atoms in bridge sites are attracted by the tip and therefore move outwards. This fact and the small increase of Fermilevel DOS associated with this relaxation leads to DOS maxima at the positions of the H atoms (Fig. 4). The DFT results therefore fully explain the STM images observed.

We can draw several conclusions from our study. Hydrogen atoms-elusive for many surface science techniques—can be imaged as protrusions with STM at low tunneling resistance. Second, and most important, STM images of mobile adsorbate structures can be deceiving with regard to structure and adsorbate coverage. Of course, H on Rh(100) is a special case due to the small difference of adsorption energies between bridge and hollow sites and due to the rather low tip-sample distance where the H atoms become visible, both factors facilitating unintentional manipulation by the STM tip. On the other hand, the H atoms reside almost in the surface plane $(\Delta z_{\text{H-Rh}} = 0.5 \text{ Å for H in hollow sites})$, whereas most other adsorbates, especially bigger molecules, protrude from the surface and are therefore more easily manipulated by the tip (cf. $R_T = 250 \text{ k}\Omega$ for CO manipulation [24]). Hence, one should always be aware of the interaction between tip and sample and the possibility of a surface modification by the tip. We should finally mention that our study also demonstrates that today's high-quality LEED studies can determine the position of H atoms and their coverage, even though H is a very weak scatterer for electrons [25].

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