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 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 × 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.