Coexistence of atomic and molecular chemisorption states: H_2/Pd(210)

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A novel H_2 molecular adsorption state on metal surfaces has been detected by temperature-programmed desorption and electron energy loss spectroscopy experiments of the H_2/Pd(210) system. The molecular nature of this state has been verified by isotope exchange experiments. This molecular state leads to a decrease of the surface work function while atomic hydrogen on Pd(210) causes an increase. *Ab initio* total-energy calculations have confirmed all experimental findings. Through these calculations the microscopic nature of this novel molecular adsorption state could be identified; it turns out that this state is stabilized by the presence of atomic hydrogen on the Pd(210) surface.

The interaction of hydrogen with metal surfaces has served as a benchmark system in surface science. Due to its relative simplicity numerous experimental and theoretical studies exist that address the energetics and dynamics of hydrogen adsorption and dissociation on metals [1–3]. These studies contributed significantly to our current understanding of the fundamental principles underlying the bond making and breaking process at surfaces. The general picture of hydrogen bonding at surfaces can be summarized as follows [1]: In general, hydrogen adsorbs dissociatively at metal surfaces. While at noble metals the dissociation is hindered by a sizable energy barrier, it occurs spontaneously at most transition metal surfaces. If molecular adsorption states exist, they are usually very weakly bound in shallow physisorption wells requiring surface temperatures below 20 K to stabilize these states [4]. At Ni(510), molecular chemisorption at surface temperatures up to 125 K has been observed, presumably at the steps, but only after the surface was passivated with a dense atomic hydrogen layer [5].

The H/Pd system is of great technological relevance due to its use as a hydrogen storage. Among other reasons, this has motivated detailed studies of the hydrogen adsorption structures and energetics [6, 7], adsorption and desorption dynamics [8–12], and poisoning phenomena [8, 10, 13]. In this Letter we report a so far unknown phenomenon in the hydrogen-surface interaction, namely the coexistence of chemisorbed molecular and atomic hydrogen on the relatively open Pd(210) surface *although the surface is not fully passivated*. By a combination of experiment and *ab initio* total-energy calculations within density functional theory (DFT) the molecular adsorption state has been clearly identified. These findings are relevant and important for the general understanding of

reactions at structured or defect-rich surfaces like in heterogeneous catalysis.

In order to investigate the hydrogen adsorption on Pd(210), temperature-programmed desorption (TPD), work-function change ($\Delta\Phi$) and high-resolution electron energy loss spectroscopy (HREELS) experiments have been performed at surface temperatures T between 50 K and 500 K in an ultrahigh vacuum (UHV) chamber with a base pressure of less than 3×10^{-11} mbar. The UHV chamber was equipped with a liquid He cryostat, a Kelvin probe for the $\Delta\Phi$ measurements, and an electron spectrometer of the Unwin type [14].

The (210) surface is a relatively open surface that, however, does not exhibit a pronounced terrace structure. The geometry of this surface is shown in Fig. 1. It is known from previous work [15] that hydrogen adsorbs atomically on Pd(210) for $T > 120$ K in three different binding states β_1, β_2, and β_3 with desorption temperatures of $\sim$180 K, $\sim$250 K, and $\sim$330 K respectively. In
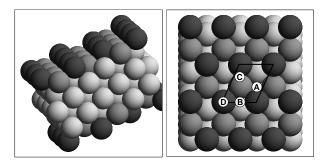

FIG. 1: Side and top view of the (210) surface. In the right panel the surface unit cell plus the three atomic adsorption sites A, B, and C are included. The site D corresponds to the molecular adsorption site.
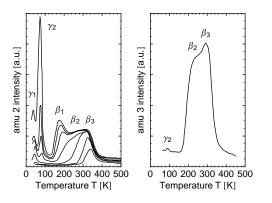
FIG. 2: Thermal desorption spectra. a) Series of H_2 TPD spectra for different exposures between 0.02 L and 0.2 L at a temperature of 50 K. b) Mass 3 (HD) TPD spectrum after a mixed H_2/D_2 exposure at 50 K.
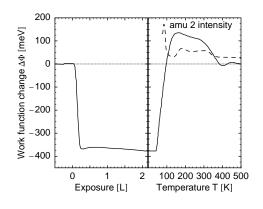

FIG. 3: Hydrogen-induced work function change $\Delta\Phi$. a) Dependence of $\Delta\Phi$ on H_2 exposure for adsorption at 50 K. b) Dependence of $\Delta\Phi$ on the surface temperature after saturation of the Pd(210) with molecular hydrogen. The H_2 TPD spectrum (dashed line, arbitrary units) is also plotted.

addition, at very high hydrogen exposures an atomic α state becomes populated which desorbs at 150 K and is attributed to subsurface hydrogen [15]. The *novel molecular* H_2 species to be described here appears in TPD spectra if the hydrogen is adsorbed at temperatures below 100 K. One typical example is given in Fig. 2a where TPD spectra for different exposures between 0.02 L and 0.2 L at an adsorption temperature of 50 K are plotted. The spectra show, in addition to the atomic β states, one intense state at 94 K with a low temperature satellite at 60 K. These states are denoted as γ_2 and γ_1 respectively.

Both states are rapidly and simultaneously filled. Saturation is attained between 0.5 and 1.0 L exposure. The spectra reveal a first order desorption kinetics and desorption energies of 155 (γ_1) and 250 meV (γ_2). In order to verify the molecular nature of the γ states, we have performed H_2/D_2 isotope exchange experiments. The Pd crystal was first exposed to $\sim$0.25 L H_2 and then to the same amount of deuterium, D_2. We then recorded the 3 amu (=HD) TPD spectrum. An HD signal in the temperature range of the γ states would indicate dissociative adsorption. But in fact, HD is almost entirely absent in this temperature range, as Fig. 2b demonstrates. However, all spectra exhibit HD signals in the temperature range of the atomic states. This indicates that not all of the atomic adsorption sites were filled by H, so that some fraction of the D_2 can dissociate either directly or upon heating during the TPD run. In another series of experiments we first exposed the crystal at temperatures above 125 K with 0.5 L of the one isotope, thus saturating the atomic states, and then at 50 K with the other isotope. The results showed no isotopic scrambling in the γ states and almost no isotope exchange in the β states.

Further details about the $H_2/Pd(210)$ interaction are revealed by the measurement of the H_2-induced work function change $\Delta\Phi$. Figure 3 shows the work function change as a function of exposure at a temperature of 50 K. After an exposure of $\sim$0.1 L, $\Delta\Phi$ drops sharply to

-370 meV, passes a shallow minimum after 0.3 L exposure and stabilizes at -375 meV after exposures of 1 L. When the hydrogen-saturated sample after an exposure of 2 L is linearly heated to 500 K with a heating rate of 1 K/s, $\Delta\Phi$ rises steeply to approximately 130 meV, the increase being completed at $\sim$120 K. On top of the $\Delta\Phi$ curve, the simultaneously recorded TPD spectrum is plotted. This spectrum demonstrates that the steep rise of $\Delta\Phi$ is associated with the desorption of the molecular H_2 adsorption state. For $T > 120$ K, $\Delta\Phi$ decreases again, with a particularly marked drop between 300 and 375 K, due to desorption of the atomic β_3 species. We have also monitored the work function change in the H_2/D_2 isotope exchange experiments. Preadsorption of the one species at $T > 120$ K, i.e., population of only the atomic adsorption states, leads to a $\Delta\Phi$ *increase* of $\sim$120 meV, and postadsorption of the other species at 50 K, i.e., population of the molecular adsorption state, causes a strong subsequent *drop* of $\Delta\Phi$.

The molecular nature of the γ states is further confirmed by HREELS results. Our data (not shown here) were taken at 50 K after admission of 0.5 L of H_2 and D_2, respectively. The H_2 spectrum shows a sharp band around 58 meV and a shoulder between 100 and 200 meV which are attributed to atomic H species [15]. In addition, we find a broad loss around 420 meV which reflects the excitation of the H-H stretching vibration. For D_2, the respective D-D vibration appears at about 300 meV as expected from the mass ratio between H and D.

The adsorption of hydrogen on Pd(210) does not lead to any superstructure in low-energy electron diffraction experiments [15]. Hence it is experimentally very difficult to identify the exact location and nature of the hydrogen adsorption states. In order to obtain this microscopic information, we have performed DFT calculations with the generalized gradient approximation (GGA) [16] using the Vienna *ab initio* simulation package (VASP) [17]. The

surface is modeled by an eleven layer slab separated by 11 Å of vacuum. Due to the use of ultrasoft pseudopotentials [18] a cutoff energy of 200 eV was sufficient to obtain converged total energies which were determined by a surface Brillouin zone integration using an 11×11 **k** point mesh. The slab together with the surface unit cell is depicted in Fig. 1. The atomic adsorption sites are denoted by A, B, and C respectively. A comparison between experimental and theoretical adsorption energies is given in Table I where the site assignment has been done according to the DFT results. The agreement between theory and experiment is indeed very satisfying.

We have then determined hydrogen dissociation paths for H_2/Pd(210) in detail. For hydrogen dissociation on the clean Pd(210) surface our main result is that at larger distances from the surface the H_2 molecule is first attracted to the top-layer Pd atom, but at closer distances it spontaneously dissociates into the A and B sites (see Fig. 1). Corresponding reaction paths have also been identified for other H_2/Pd systems [7, 19]. This means that at the clean Pd(210) surface no stable molecular adsorption state exists.

A re-examination of the TPD spectra in Fig. 2a reveals that indeed for very small exposures (< 0.03 L) only atomic β states become populated. We have therefore determined hydrogen dissociation paths on hydrogen-precovered Pd(210). It turns out that the hydrogen dissociation into the A and C sites is hindered by a barrier of about 220 meV if all B sites are populated with H atoms. However, the attraction of the H_2 molecule to the top-layer Pd atom (site D in Fig. 1b) is hardly influenced by the presence of the preadsorbed H atoms. Thus a metastable molecular adsorption state with a well depth of 270 meV is formed. This state is illustrated in Fig. 4 in a so-called elbow plot of the potential energy surface (PES) as a function of the H_2 center-of-mass distance z
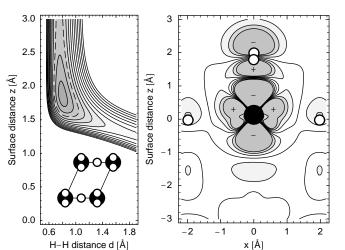

FIG. 4: DFT results of the H_2 molecular adsorption on the hydrogen-covered Pd(210) surface. a) Contour plot of potential energy surface. The coordinates in the figure are the H_2 center-of-mass distance from the surface z and the H-H interatomic distance d. The lateral H coordinates are indicated in the inset. The contour spacing is 0.1 eV, and the vacuum energy level is marked by the dashed contour line. b) Electron density difference plot of the molecular adsorption state in the x-z plane. The positions of the H atoms and the top Pd atom are marked by open and filled circles respectively.

and the H-H distance d for molecules approaching on top of the top-layer Pd atoms adjacent to the B sites.

Even for atomic hydrogen coverages of $\theta = 2$ and 3 H_2 molecular adsorption wells on top of the first layer Pd atom are still present with adsorption energies of 220 and 90 meV, respectively. We associate the molecular wells for $\theta = 1$ and 2 with the γ peaks in the TPD spectra. This means that the two γ peaks do not correspond to two different molecular adsorption sites or states, but just to two different underlying atomic hydrogen coverages (see Table I). In Fig. 2 no molecular adsorption state corresponding to $\theta = 3$ can be resolved since the adsorption temperature was too high. However, for longer exposures at 30 K an additional molecular state (δ) can be identified between 30 and 40 K as a shoulder in the TPD spectrum which we attribute to this particular state.

Our calculations also confirm the experimental trend in the work function change upon hydrogen adsorption. While atomically adsorbed hydrogen increases the work function by up to 250 meV according to the DFT results, additional molecular hydrogen leads to a work function decrease of more than 700 meV which is somewhat larger than in the experiment. Furthermore, the DFT calculation yields an H-H stretch frequency in the γ_1 state of $\hbar\omega_{vib} = 422$ meV, which is rather close to the HREELS results of 420 meV.

The good agreement between experiment and theory confirms that we have identified the correct molecular adsorption state. In Fig. 4b an electron density difference

| coverage | $E_{ad}(H)$ [eV] | | | | $E_{ad}(H_2)$ [eV] | | | |
	state	site	exp.	theory	state	site	exp.	theory
$\theta = 1$	β_3	B	0.41	0.42	γ_2	D	0.25	0.27
$\theta = 2$	β_2	B,A	0.33	0.30	γ_1	D	0.16	0.22
$\theta = 3$	β_1	B,A,C	0.23	0.16	δ	D	–	0.09

TABLE I: Atomic and molecular adsorption energies as a function of hydrogen coverage on Pd(210). The atomic adsorption energies are defined as the energies for additional adsorption of one H atom per surface unit cell with respect to the H_2 molecule in the gas phase. The experimental results have been derived from TPD spectra. The theoretical results were obtained by fully relaxing the adsorbates and the first five Pd layers to their minimum energy configuration. The molecular energies $E_{ad}(H_2)$ correspond to the molecular adsorption on site D at a surface precovered with atomic hydrogen with the atomic hydrogen coverage per unit cell specified by θ. The notation of the sites refers to Fig. 1.

plot of this state is shown. It corresponds to the density difference between the interacting system and the isolated H_2 molecule and the H-covered Pd(210) surface. The plot demonstrates the strong hybridization between the H_2 molecule and the Pd(210) surface which is mainly due to the interaction of the Pd d_{z^2} with the H_2 σ orbital and the interaction of the Pd d_{xz} and d_{yz} with the H_2 σ^* orbital [19]. The H_2 molecule becomes strongly polarized thus decreasing the work function. On the other hand the molecular bond is weakened only slightly. The preadsorbed H atoms at the bridge site are located at the same height as the top layer Pd atoms. Their presence does not significantly disturb the H_2 interaction with the top layer atoms at H_2 distances of more than 1.6 Å. However, these preadsorbed H atoms do hinder the dissociation of further H_2 molecules at the surface. They thus stabilize the molecular adsorption state.

The following scenario for the hydrogen desorption on Pd(210) can be derived from the combination of experimental and theoretical results. On clean Pd(210), hydrogen adsorbs dissociatively. Once atomic hydrogen is present on the Pd(210) surface, further hydrogen dissociation becomes kinetically hindered close to the adsorbed hydrogen atoms *although atomic adsorption sites are still available.* This can be regarded as a local self-poisoning of hydrogen dissociation. In Fig. 3 almost no initial increase of the work function upon atomic hydrogen adsorption can be detected due to the low coverage that does not produce any significant work function change, but we always find a pronounced initial increase in the work function, in particular for smaller hydrogen fluxes. At higher coverages the work function change is then dominated by the strong decrease caused by the adsorbed H_2 molecules. A similar scenario might also be valid for the adsorption of hydrogen on stepped Ni surfaces such as the one studied in Ref. [5] which we are planning to check by studying the system H_2/Ni(210).

Interestingly enough, Fig. 2a) shows that the weaker bound γ_1 state becomes populated first. This corresponds to H_2 adsorption on a Pd(210) surface with two hydrogen atoms per surface unit cell. One might speculate that apparently the first dissociated H atoms stay within one unit cell, i.e., the single H atoms are not very mobile after dissociation and end up in the nearest available adsorption sites that do not correspond to the most stable ones. This means that at an adsorption temperature of 50 K the population of the atomic adsorption states is not in thermal equilibrium. This view is supported by the fact that at an adsorption temperature of 100 K, which apparently allows to be closer to thermal equilibrium, the weakly bound β_1 state appears only at an exposure of 1.0 L [15], i.e., for the exposures corresponding to the spectra of Fig. 2a) it is not populated. Further evidence comes from the findings that the ratio of the γ_1 to the γ_2 peak depends sensitively on the specific adsorption conditions of the experiment. On the other hand, the largest exposure shown in Fig. 2a), 0.2 L, does not correspond to the saturation of all the atomic states so that γ_2 states can still be populated.

In conclusion, by a combination of experiment and theory we have identified a *novel molecular* chemisorption state of H_2 on Pd(210) with a binding energy of ~ 250 meV. This state is stabilized by the presence of atomic hydrogen at the surface. The preadsorbed atomic hydrogen does not significantly disturb the interaction of the H_2 molecules with the Pd atoms as long as the H_2 molecules are further away from the surface, but it hinders the H_2 dissociation on Pd(210) although atomic adsorption sites are still available.

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