## Identification of new adsorption sites of H and D on rhodium(100)

G. Pauer

Institute of Solid State Physics, University of Technology Graz, Petersgasse 16, A-8010 Graz, Austria

A. Eichler

Institute of Material Science, University of Vienna, Sensengasse 8, A-1090 Wien, Austria

M. Sock, M. G. Ramsey, and F. Netzer

Institute of Experimental Physics, University of Graz, Universitätsplatz 5, A-8010 Graz, Austria

A. Winkler<sup>a)</sup>

Institute of Solid State Physics, University of Technology Graz, Petersgasse 16, A-8010 Graz, Austria

(Received 7 May 2003; accepted 10 June 2003)

Exposure of Rh(100) to hydrogen (deuterium) in atomic form leads to the population of adsorption sites, not attainable with molecular species. Quantitative thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations have been applied to investigate these new adsorption sites. In addition to the fourfold hollow sites (1 ML), which can be populated by dissociative adsorption, occupation of subsurface sites and the population of additional surface sites (for deuterium) have been observed (maximum coverage 3.4 ML). In TDS individual adsorption states show up in the form of three different peaks: Recombination of H (D) atoms from hollow sites around 300 K, desorption of subsurface species between 150–200 K, and recombinative desorption via a molecular precursor at about 120 K (for deuterium only). The exposure of the Rh(100) surface to atomic H (D) leads to a pronounced roughening of the surface, as evidenced in the HREELS spectra. Zero point corrected adsorption energies, activation barriers for adsorption, desorption, and diffusion into the subsurface sites, as well as vibrational energies have been calculated by DFT for a variety of adsorbate configurations of H and D and compared with the experimental data. © 2003 American Institute of Physics. [DOI: 10.1063/1.1597196]

## I. INTRODUCTION

The interaction of rhodium single-crystal surfaces with small molecules such as  $H_2(D_2)$  has been studied extensively, not only because of the relative simplicity of this system, but also because of its relevance to heterogeneous catalysis. The essential results of numerous experimental<sup>1-9</sup> as well as theoretical studies<sup>10–15</sup> can be summarized as follows: (i) the saturation coverage of dissociatively adsorbed hydrogen on the rhodium (100) surface was supposed to be 1 monolayer (ML) for adsorption at 100 K, with all hydrogen atoms located in the fourfold hollow positions;<sup>5</sup> (ii) the desorption energy at low coverage was determined to be 19-23 kcal/mol;<sup>4,8</sup> (iii) both, the desorption energy and the preexponential factor were found to decrease with coverage. Many comparisons have been drawn with the adjacent transition metal palladium with respect to the adsorption and desorption behavior.<sup>10,15</sup> Contrary to the system hydrogenpalladium, subsurface absorption of hydrogen in rhodium has been considered as improbable, because of the weak stability of bulk rhodium-hydride.<sup>16,17</sup> Recent STM studies of H on Rh(100) have given peculiar results,<sup>18</sup> suggesting the occupation of bridge sites and a saturation coverage of 2 ML. However, it has been shown that the observed bridge position of the adsorbed hydrogen atoms was influenced by the tip of the STM, due to small energy differences between adsorption at bridge sites and fourfold hollow sites.

In this work we focus on the population of individual adsorption sites of H and D on Rh(100), using both molecular and atomic species for exposure. New features have been observed in the temperature programed desorption (TPD) spectra, indicating the population of further surface and subsurface sites, in addition to hollow sites, by dosing with atomic hydrogen and deuterium. Coadsorption and abstraction experiments as well as HREELS investigations have been performed to identify and characterize these new adsorption sites. Detailed DFT calculations have been carried out as well, to support the conclusions drawn from the experimental results.

## **II. EXPERIMENTAL DETAILS**

The UHV system used for the temperature programed desorption experiments is equipped with LEED (low energy electron diffraction), AES (Auger electron spectroscopy), a multiplexed mass spectrometer, an extractor ion gauge (calibrated with the help of a spinning rotor gauge<sup>19</sup>), and a doser for atomic hydrogen. The doser basically consists of an electron beam heated tungsten capillary, designed after the concepts of Bischler and Bertel.<sup>20</sup> At a capillary temperature of about 2000 K, a nearly complete dissociation of the effusing hydrogen can be obtained. A detailed characterization of this

0021-9606/2003/119(10)/5253/14/\$20.00

5253

<sup>&</sup>lt;sup>a)</sup>Electronic mail: a.winkler@tugraz.at

doser was performed by Eibl et al.<sup>21</sup> During exposure to atomic hydrogen (deuterium) the sample was positioned in front of the doser capillary with a normal angle of incidence. The circular Rh(100) single-crystal sample (7 mm diameter) was spot welded to molybdenum wires for resistive heating and mounted on a LN<sub>2</sub> cooled sample holder. The purity of the sample surface was ensured by regular sputtering with Ar<sup>+</sup> ions at 900 K and annealing at 1020 K for 45 min. Thermal desorption was carried out, starting from the adsorption temperature of 97 K up to a final temperature of 670 K, with a linear heating rate of 3 K/s. For quantitative evaluation of the thermal desorption spectra a calibration device as described in Ref. 22 was used. Quantitative TPD additionally requires an accurate determination of the relevant adsorption area which contributes to adsorption/desorption. For this reason, all sample surfaces were first covered with an oxygen passivation layer according to a procedure described by Thiel *et al.*,<sup>23</sup> to inhibit dissociative adsorption of  $H_2$ . By sputtering the front side of the sample and thus selectively removing the oxygen passivation layer, subsequent adsorption and desorption could be attributed to the front side only. Care has also to be taken in the quantitative determination of the number of impinging particles by using a hot doser. A detailed description of the experimental procedures to be applied for quantitative H (D) dosing can be found elsewhere.<sup>21,24</sup>

The HREELS experiments have been performed in a separate, custom-designed three-level UHV chamber. The chamber was equipped with a four-grid LEED optics, used for both LEED and Auger spectroscopy, a mass spectrometer, a doser for atomic hydrogen, and an ErHREELS31 spectrometer. The spectrometer is a double-monochromator double-analyzer construction using toroidal condensers for the energy-selective elements. An incidence angle of  $60^{\circ}$  to the surface normal and a primary beam energy of 5.5 eV were used, with the scattering plane along the [100] direction. Varying the primary energy did not change the spectra significantly. The analyzer could be rotated around the sample for off-specular measurements. The resolution in the spectra presented here was typically 4 meV, as measured from the FWHM of the elastically scattered electrons from the hydrogen-covered Rh(100) surface.

The Rh(100) crystal was cleaned by  $Ar^+$  sputtering at room temperature and subsequent annealing at 1400 K for a few minutes, to restore the surface order. Then, the crystal was heated in  $1 \times 10^{-7}$  mbar oxygen to remove the residual carbon contamination. After flashing to 1300 K to remove the excess oxygen, a sharp  $(1 \times 1)$  LEED pattern was obtained. Molecular hydrogen exposure was performed with the sample in front of the tungsten capillary which was also used for atomic hydrogen dosing. The high effective hydrogen pressure in front of the capillary should ensure a Rh(100) surface with a hydrogen coverage close to saturation (1.22 ML) and minimize CO adsorption from the residual gas during the dosing. In order to remove adventitious CO adsorbed on the surface prior to the hydrogen exposure, for the HREELS experiments the sample was flashed to 600 K and subsequently cooled down to 150 K within the hydrogen flux. In the case of atomic H (D) dosing a coverage of approximately 2.3 ML was established.



FIG. 1. Thermal desorption spectra (TDS) of  $H_2$  and  $D_2$  on Rh(100), following molecular exposure. Heating rate  $\beta$ =3 K/s. The thick black line corresponds to the saturation coverage  $\Theta(H_2, \text{sat.}) = 1.22 \text{ ML} \pm 10\%$  [thin black line:  $\Theta(H_2) = 1.0 \text{ ML}$ ] and the thick gray line to  $\Theta(D_2, \text{sat.})$ = 1.21 ML±10%. The dotted lines correspond to the following hydrogen coverages: 0.19, 0.27, 0.39, 0.53, 0.78 ML.

# III. EXPERIMENTAL RESULTS—TEMPERATURE PROGRAMED DESORPTION (TPD)

## A. Molecular $H_2/D_2$ exposure on Rh(100)

The first issue to be addressed in this paper concerns the saturation coverage of hydrogen and deuterium on Rh(100), when theses species are dosed in molecular form. The sample was exposed repeatedly to different amounts of molecular hydrogen (deuterium) (isotropic exposure), and the respective thermal desorption spectra (TDS) have been analyzed quantitatively, as described in Ref. 22. In Fig. 1(a) series of desorption spectra as function of different molecular hydrogen exposure is presented. For comparison, the saturation desorption spectrum for deuterium is also shown (gray line). The line shapes and the characteristic desorption temperatures of the TDS proved to be in good agreement with those presented in previous work,<sup>4,8</sup> including the inverse kinetic isotope effect (KIE) for the  $\beta_1$  state (deuterium desorbs earlier than hydrogen), as mentioned in Ref. 8. The small desorption peak at 120 K, on the other hand, which we designate as  $\alpha$  peak, shows a normal isotope effect. In addition, a broad shoulder appears for saturation at the left-hand side of the  $\beta_1$  peak. Note that the nomenclature for the individual desorption peaks as used in this work deviates somewhat from that in Ref. 8.

Whereas good agreement exists with the literature data for the qualitative features of the desorption spectra, there is disagreement between the saturation coverage determined in this work, and the so far accepted saturation coverage of 1.0 ML  $(1.39 \times 10^{15} \text{ atoms/cm}^2)$ .<sup>3,5</sup> Careful calibration of the coverage by the methods outlined in the Experiment section yields a saturation coverage of 1.22 ML ±10%, both for hydrogen and deuterium. The spectra for hydrogen saturation (1.22 ML) and for 1.0 ML are drawn as thick and thin black lines in Fig. 1, respectively. One clearly sees that the  $\alpha$  peak and the shoulder of the  $\beta_1$  peak start to develop significantly only for a coverage above 1 ML. From additional quantitative analysis of the exposure-coverage data, an initial stick-



FIG. 2. Thermal desorption spectra (TDS) of H<sub>2</sub> after dosage of atomic H on Rh(100). Heating rate  $\beta$ =3 K/s. The hydrogen coverages of the corresponding curves are as follows: (a) 1.06 ML; (b) 1.90 ML; (c) 2.27 ML; (d) 2.68 ML; (e) 3.02 ML. The hydrogen saturation spectrum following molecular exposure [curve (f)] is shown as a dotted line for comparison.

ing coefficient of  $S_0 = (0.85 \pm 0.15)$  could be deduced for adsorption of molecular hydrogen and deuterium on Rh(100), which is in nice agreement with theoretical predictions.<sup>13</sup> A nearly constant sticking coefficient up to about 0.5 monolayers indicates dissociative adsorption via a precursor state.<sup>4</sup>

## B. Atomic hydrogen exposure on Rh(100)

Exposure of the clean rhodium surface to increasing amounts of atomic hydrogen via the Bertel-type doser<sup>20</sup> resulted in the significant population of a new adsorption site. The thermal desorption spectra in Fig. 2 [curves (a)–(e)] show the rise of a new peak for a coverage exceeding the saturation coverage for dissociative adsorption [Fig. 2, curve (f)], which we designate as  $\beta_2$  peak. The change of the hydrogen coverage as a function of the exposure to atomic hydrogen is presented in Fig. 3 (open squares). In addition, the coverage curve for molecular hydrogen exposure is shown for comparison (open triangles). Given the already high initial sticking coefficient for dissociative H<sub>2</sub> adsorption



FIG. 3. Coverage vs exposure relationship for adsorption of molecular  $H_2$  (triangles), atomic H (squares), and atomic D (full circles) on Rh(100).  $N_i$  represents the actual number of impinging H/D atoms during exposure.



FIG. 4. Thermal desorption spectra (TDS) after dosage of atomic D on Rh(100). Heating rate  $\beta$ =3 K/s. The deuterium coverages of the corresponding curves are as follows: (a) 1.55 ML; (b) 1.90 ML; (c) 2.30 ML; (d) 2.94 ML. The deuterium saturation spectrum following molecular exposure [curve (e)] is shown as a dotted line for comparison. The inset again shows curves (d) and (e) for better comparison of the peak heights.

 $(S_0 = 0.85)$ , a sticking coefficient of  $S_0 \approx 1.0$  is a reasonable assumption for adsorption of H (D) atoms on Rh(100). Concerning the actual number of incident H (or D) atoms during exposure, it should be pointed out that as long as the current coverage does not exceed the saturation for molecular  $H_2$  (or  $D_2$ ) exposure, dissociative adsorption from the background adds to the amount of directly adsorbed atomic H (or D) from the doser. Note that the term "exposure" does not have the same meaning in the case of atomic dosing, because a mixture of directly impinging atoms and molecules from the isotropic background contributes to the total amount of impinging particles. The abscissa in Fig. 3 gives the total number of impinging atoms, independent of their angle of incidence and independent of their state in the gas phase (molecules or atoms). The nonvanishing slope of the coverage curve for atomic exposure in Fig. 3 indicates that the highest coverage of 3.4 monolayers obtained in this experiment is not the upper limit. Adsorption on the edges and on the backside of the sample can be largely ruled out because only the front side of the sample is exposed to atomic hydrogen, and the density of atomic hydrogen in the isotropic gas phase is exceedingly small. Therefore, adsorption on additional surface sites (bridge, on-top) and/or absorption in subsurface sites (octahedral) is necessary to explain this result. As we will show in Sec. VII B, the  $\beta_2$  peak can be attributed to subsurface hydrogen.

## C. Atomic deuterium exposure on Rh(100)

With regard to the subsequent H–D abstraction experiments, the same thermal desorption experiments as described in the previous section for hydrogen have been repeated with atomic deuterium. In Fig. 4, a series of thermal desorption spectra with increasing exposures to atomic deuterium is presented [curves (a)–(d)]. For comparison, the saturation coverage as obtained with molecular exposure is shown as dotted line [curve (e)]. The additional  $\beta_2$  peak, due to atomic exposure as observed for hydrogen, also shows up for deuterium exposure. However, in this case an additional sharp



FIG. 5. Thermal desorption spectra (TDS) of H<sub>2</sub>, D<sub>2</sub>, and HD, after exposure to different amounts of atomic D on the hydrogen precovered Rh(100) surface. Heating rate  $\beta$ =3 K/s. In panel (a), the TDS of the initial hydrogen coverage [ $\Theta_i$ (H)=2.3 ML] is shown as a thin black line. The individual D exposures for (a) through (d) can be deduced from Fig. 6.

desorption peak ( $\alpha$  peak) appears at 125 K for a coverage exceeding 1.2 ML. This peak seems to be of zero-order kinetics, shifting from 125 K to slightly higher temperatures with increasing coverage. The maximum area of this peak [curve (d) in Fig. 4 and inset] corresponds to about 0.6 ML. Interestingly, coadsorption experiments, as presented in the next section, have specified this feature as a pure surface peak. The deuterium coverage as a function of atomic D exposure is also shown in Fig. 3 (full circles). Despite the obvious difference of the TDS features for deuterium compared to those obtained with atomic hydrogen, the coverage versus exposure data of atomic D follows closely those of atomic H. It is also necessary in this context to mention previous investigations of coadsorption of D<sub>2</sub> and H<sub>2</sub> with CO on rhodium (100),<sup>3,6</sup> where similar TDS features exhibiting a sharp desorption peak at about 150 K have been found. We have therefore performed several coadsorption experiments with atomic deuterium (hydrogen) and CO, where we could clearly distinguish between the influence of coadsorbed CO and the effect of interest, caused by the atomic deuterium itself. In the present case, the residual amount of adsorbed CO was far too small to induce desorption of deuterium as a sharp peak in the low temperature regime by a rearrangement of the CO+H/D layer, as suggested by Richter et al.<sup>6</sup> We would like to emphasize therefore, that the sharp deuterium desorption peak observed at 125 K is a feature of pure deuterium adsorption. The difference of the desorption behavior between deuterium and hydrogen in the low temperature regime is an isotope effect, which will be addressed in the Discussion.

### D. H/D coadsorption and abstraction experiments

To find evidence for the existence of subsurface-bound hydrogen (deuterium), a series of coadsorption/abstraction experiments with atomic hydrogen and deuterium has been performed (at a sample temperature of  $\sim 100$  K). At first, the clean rhodium surface was exposed to atomic hydrogen up to an initial coverage of 2.3 ML, in order to occupy adsorption sites in addition to the fourfold hollow sites. The TDS of this initial situation is shown in Fig. 5(a) as a thin black line. In a second step, the surface was exposed to atomic deuterium. As soon as the sample was turned into the atomic beam, the appearance of HD and some  $H_2$  in the gas phase indicated that Eley-Rideal abstraction and collision induced reactions took place, as observed for other H-metal surface systems.<sup>25,26</sup> Actually, it has been shown both experimentally (e.g., Ref. 27 and other work by the Küppers group) and theoretically (e.g., Ref. 28 and other work by Jackson and Persson) that in many cases the HD abstraction is not a pure Eley-Rideal process but rather a Harris-Kasemo process,<sup>29</sup> in which a hot H-atom precursor is involved in the abstraction reaction. The depleted adsorption sites are immediately refilled by deuterium, and some D atoms also penetrate into subsurface sites. The basic idea of this experiment is that in the abstraction process only species adsorbed on the surface will be removed significantly and H atoms possibly located in subsurface sites will be removed with much lower probability. After some time the atomic deuterium exposure was stopped and multiplexed thermal desorption spectra of H<sub>2</sub>, HD, and  $D_2$  were taken with the calibrated mass spectrometer. Figure 5(a) shows the result after very small D postexposure. It is evident that the  $\beta_1$  peak of H<sub>2</sub> decreased significantly, whereas the  $\beta_2$  peak decreased only slightly. With increasing postexposure to atomic D the H<sub>2</sub>  $\beta_1$  peak vanishes completely, and also the  $\beta_2$  peak starts to decrease slowly [H<sub>2</sub> curves in Figs. 5(b), 5(c)]. Finally, after large D exposure the main desorbing species is again molecular deuterium, showing all the features of pure D adsorption [curve  $D_2$  in Fig. 5(d)]. The most interesting aspect in this case is the appearance of the  $\alpha$  peak in the D<sub>2</sub> spectrum [see Figs.



FIG. 6. H and D coverages as a function of atomic D exposure on the hydrogen precovered Rh(100) surface. The initial hydrogen coverage was  $\Theta_i(H) = 2.3$  ML, as indicated by the circle. The corresponding TDS of the marked data points (a)–(d) are shown in Figs. 5(a)–5(d).

5(c)-5(d)]. The fact that no intermixed HD species are found, which contribute to the  $\alpha$  peak, suggests that the desorbing D<sub>2</sub> molecules originate from the recombination of deuterium atoms *on the surface only*. Figure 6 summarizes the change of the total H and D coverage versus D exposure, as calculated from the integrated and calibrated H<sub>2</sub>, HD, and D<sub>2</sub> spectra. For small atomic D postexposures a fast decrease of the H coverage can be seen, but as soon as the initial coverage of 2.3 ML is reduced to about 1.3 ML [Fig. 6, label (b)] further abstraction proceeds much more slowly. As one can see in the corresponding TDS in Fig. 5(b), the sudden reduction of the HD abstraction efficiency coincides with the disappearance of the  $\beta_1$  peak in the H<sub>2</sub> desorption spectrum.

The same abstraction experiments have also been performed with reversed order of the isotopes: Starting with an initial deuterium coverage of 2.0 ML [Fig. 7(a), thin black



FIG. 8. H and D coverages as a function of atomic H exposure on the deuterium precovered Rh(100) surface. The initial deuterium coverage was  $\Theta_i(D) = 2.0$  ML, as indicated by the circle. The corresponding TDS of the marked data points (a)–(c) are shown in Figs. 7(a)–7(c).

line] the sample was postdosed with atomic hydrogen. Already after a very short H postexposure the  $\beta_1$  peak as well as the  $\alpha$  peak were significantly reduced [Fig. 7(a)]. The fact that the  $\alpha$  peak is effectively abstracted again supports the idea that this peak is due to recombination of a *surface species*. The summarized H and D coverage versus H exposure are shown in Fig. 8. All the features are qualitatively the same as for the experiment with reversed isotopes.

## IV. EXPERIMENTAL RESULTS—HREELS INVESTIGATIONS

The vibrational spectra of the surfaces investigated are presented in Fig. 9. Curve (a) displays the loss spectrum obtained after exposing the Rh(100) surface to molecular hydrogen at 100 K up to saturation coverage. Hydrogen is known to adsorb dissociatively in the fourfold hollow sites



FIG. 7. Thermal desorption spectra (TDS) of H<sub>2</sub>, D<sub>2</sub>, and HD, after exposure to different amounts of atomic H on the deuterium precovered Rh(100) surface. Heating rate  $\beta \sim 3$  K/s. In panel (a), the TDS for the initial deuterium coverage [ $\Theta_i$ (D) = 2.0 ML] is shown as a thin black line. The individual H exposures for (a) through (c) can be deduced from Fig. 8.



FIG. 9. High resolution EELS spectra of Rh(100) after dosing (a) molecular  $H_2$  (1.2 ML); (b) atomic H (2.3 ML); and (c) atomic D (2.3 ML). All exposures have been performed at 100 K. The inset shows the intensity of the elastically reflected primary peak for different surface treatments (see the text).

on the Rh(100) surface, as evidenced by the distinct vibrational feature at 84 meV. This peak can be associated with the Rh-H stretching vibration and has also been reported in the literature.<sup>5–7</sup> The two peaks at 235 and 255 meV are due to the C-O stretching vibrations of adventitious carbon monoxide adsorption in bridge and on-top positions, respectively.<sup>7</sup> Since the intramolecular C–O stretching vibration has a very large dynamic dipole moment, even small amounts of adsorbed CO appear quite prominently in the vibrational spectrum. The spectrum after the exposure to atomic hydrogen is significantly different from the one obtained after molecular dosage, as seen in Fig. 9(b). The loss feature at 84 meV is replaced by a broad structure with the center of mass at about 50 meV and a large tail to higher loss energies, and a broad structure at around 130 meV. Furthermore, a vibrational mode at 200 meV has developed. As an additional effect of the atomic hydrogen exposure the adsorption of CO in the on-top site is suppressed, while the bridge-bonded CO intensity remains unchanged.

In order to facilitate the peak assignment, experiments were also performed with atomic deuterium. The loss spectrum of Fig. 9(c) shows that the 200 meV feature, which has been observed for atomic hydrogen dosing, has shifted to 150 meV. Taking into consideration a  $\sqrt{2}$  vibrational fre-

quency shift due to the mass difference between hydrogen and deuterium, this mode is identified as a hydrogen vibration. Similar shifts are observed for the broad structure around 130 meV and the peak at 50 meV.

The intensity of the primary peak, i.e., the number of elastically scattered electrons per time unit, can be considered as a measure of the reflectivity of the surface and hence of the surface order. Molecularly offered hydrogen forms a  $(1 \times 1)$  overlayer which tends to increase the reflectivity and hence the elastic count rate by about one third (Fig. 9, inset). A similar effect has also been reported by Richter et al.<sup>7</sup> Atomic hydrogen, in contrast, seems to roughen the surface to a large extent, as concluded from the dramatic drop of the primary intensity by a factor of 20. The surface roughening due to atomic hydrogen exposure is also observable in LEED, where the sharp integral-order spots of the clean surface become very diffuse, with an intense background characteristic of a rough surface. Note that the surface morphology is also reflected in the behavior of the elastic count rate when the angular position of the analyzer is varied. In the case of molecular hydrogen dosing the primary intensity decreases rapidly when the analyzer is moved away from the specular direction, which is characteristic of high surface reflectivity. Atomic hydrogen exposure, however, results in a primary intensity which is independent of the analyzer position within a broad angular range. This is further evidence for the surface roughening after atomic hydrogen treatment.

The thermal evolution of a Rh(100) surface exposed to atomic H as seen in HREELS is shown in Fig. 10(A). A similar heating sequence has also been carried out after deuterium exposure [see Fig. 10(B)], and similar effects as described below for the hydrogen case are observed. The first heating step [150 K, Fig. 10(A), curve (b)] does not modify the vibrational spectrum significantly. On heating to 230 K, however, major differences can be detected [Fig. 10(A), curve (c)]. In particular, the loss energy range from 20 to 100 meV is affected most, as evident from an overall reduction of intensity within this regime. This is most clearly seen in the inset of Fig. 10(A). These spectral changes are difficult to quantify because of the overlap with the frustrated CO translations perpendicular to the surface, which are also located in the region around 50 meV. According to Richter et al.,<sup>7</sup> the CO thermal desorption has its maximum at 500 K. The intensity reduction around 50 meV is therefore not due to the removal of carbon monoxide from the surface, but has to be correlated mainly with desorbing hydrogen species. The other remarkable point after this heating step to 230 K is the disappearance of the hydrogen-associated peak at 200 meV. Finally, a band at around 110 meV starts to emerge, which develops into a sharp peak upon heating to room temperature. The surface species responsible for this peak could not be identified so far, but it disappears again after heating the surface to 500 K [see Fig. 10(A), curve (e)]. This last heating step results in a loss spectrum without any hydrogen-derived structures. Obviously the surface has been cleaned from the adsorbed hydrogen species, but is still very rough, as one can see in the inset of Fig. 9. The primary beam intensity, which has dropped dramatically after the atomic hydrogen dosing,



FIG. 10. (A) High resolution EELS spectra after dosing 2.3 ML atomic H on Rh(100) at 100 K (a), and subsequent heating to (b) 150 K; (c) 230 K; (d) 300 K; and (e) 500 K. The inset displays the thermal evolution in the energy loss range 20-100 meV with extended scales. (B) High resolution EELS spectra after dosing 2.3 ML atomic D on Rh(100) at 100 K (a), and subsequent heating to (b) 150 K; (c) 230 K; (d) 300 K; and (e) 500 K.

remains low even after heating to 900 K. The surface roughness could only be removed by annealing at 1400 K, where the original surface order could be re-established. The loss spectra of Fig. 10(B), recorded after the Rh(100) surface was exposed to atomic D at 100 K, confirm the pattern discussed for the H-exposed Rh(100) surface. Heating to 150 K has little effect [curve (b)], but heating to 230 K removes the D-induced structure at 150 meV [curve (c)]. After heating to 500 K all structures have disappeared apart from a small peak at 250 meV, which is due to readsorption of a small amount of on-top CO from the background atmosphere.

## V. FUNDAMENTALS OF THEORETICAL MODELING

Density functional theory (DFT) calculations have been carried out with the VIENNA AB INITIO SIMULATION PACKAGE (VASP).<sup>30–32</sup> VASP is a plane wave-based density functional code employing the projector augmented wave method.<sup>33</sup> A cutoff energy for the expansion of the plane waves of 250 eV was found to be sufficient for an accurate description. For exchange and correlation, generalized gradient corrections (GGA) according to Perdew et al.<sup>34</sup> were applied. Although this functional underestimates the binding energy of the free molecule (without zero-point energies) by 183 meV (4.544 eV, compared to 4.727 eV), it was shown in the past that energy differences between various adsorption configurations can be determined with much higher accuracy. This is related to the fact that the local density approximation (also in its gradient-corrected form) works best for systems with small density gradients. The calculation of binding energies, however, requires the calculation of a free spin-polarized H atom and the free-H<sub>2</sub> molecule, both systems where this is not fulfilled. For adsorbate systems on the other side, the energy of the molecule is only used as reference and any error in the total energy of the molecule means only a shift in the adsorption energy, and most errors due to the density gradient at the surface cancel out when comparing the energies of similar adsorption structures.

The rhodium (100) surface was modeled by an eightlayer slab, separated in z direction by a vacuum equivalent to seven substrate layers. Most of the calculations were performed with a  $p(2\times2)$  cell containing four atoms per layer, the positions of which were fully optimized for the surface and subsurface layer. The Brillouin zone was sampled by a grid of (5×5) k points. Adsorbate frequencies were calculated from the forces due to finite displacements ( $\Delta = \pm 0.03$ Å) of each of the H atoms in all Cartesian coordinates. On the basis of these frequencies zero point energies have been calculated. For the calculation of diffusion and dissociation barriers a transition state search with the nudged elastic band method was performed.<sup>35</sup>

## VI. RESULTS—DFT CALCULATIONS

Using the setup described in the previous section, numerous calculations for configurations with on-surface and subsurface hydrogen were performed. The chosen  $p(2 \times 2)$  unit cell determines the periodicity of the investigated configurations, and hence limits the accessible adsorbate coverages to multiples of 0.25 ML.

TABLE I. Zero point energies  $(E_0^H, E_0^D)$ , adsorption energies  $(E_{ads})$ , and zero point corrected adsorption energies  $(E_{ads}^H, E_{ads}^D, \text{ compare the text})$  for various adsorption configurations of H and D (all energies in meV/atom). Zero point energy for the free molecules H<sub>2</sub>: 133 meV/atom D<sub>2</sub>: 94 meV/ atom.

| Coverage | Sites   | $E_0^{\mathrm{H}}$ | $E_0^D$ | Eads | $E_{ads}^{\rm H}$ | $E_{ads}^{D} \\$ |
|----------|---------|--------------------|---------|------|-------------------|------------------|
| 0.25     | 1h      | 100                | 71      | 535  | 568               | 558              |
|          | 1b      | 160                | 113     | 536  | 509               | 517              |
| 0.50     | 2h      | 103                | 72      | 541  | 572               | 563              |
| 0.75     | 3h      | 103                | 73      | 535  | 566               | 557              |
| 1.00     | 4h      | 104                | 74      | 539  | 568               | 559              |
|          | 4b      | 167                | 118     | 517  | 483               | 493              |
| 1.25     | 4h + 1b | 128                | 90      | 428  | 433               | 432              |
|          | 5b      | 174                | 123     | 477  | 436               | 448              |
|          | 4h + 1t | 122                | 86      | 447  | 458               | 454              |
|          | 4h+1o   | 113                | 80      | 388  | 409               | 403              |
| 1.50     | 4h+2b   | 139                | 98      | 356  | 350               | 351              |
|          | 6b      | 180                | 127     | 434  | 388               | 401              |
|          | 4h+2t   | 135                | 95      | 392  | 390               | 391              |
|          | 4h+2o   | 116                | 82      | 277  | 294               | 289              |
|          | 4h+1mol | 134                | 95      | 374  | 373               | 373              |
| 1.75     | 4h+3b   | 143                | 101     | 301  | 292               | 295              |
|          | 7b      | 185                | 131     | 429  | 377               | 393              |
|          | 4h+3t   | 142                | 100     | 329  | 320               | 323              |
| 2.00     | 4h+4b   | 164                | 116     | 261  | 230               | 239              |
|          | 8b      | 193                | 137     | 414  | 354               | 371              |
|          | 4h+4t   | 146                | 103     | 290  | 278               | 281              |
|          | 4h+2m   | 148                | 105     | 292  | 277               | 281              |
|          |         |                    |         |      |                   |                  |

#### A. Energetics

The adsorption energy  $(E_{ads})$  of a particular configuration determines the average energy gain per adsorbate with respect to the gas phase, and is given by

$$E_{\text{ads}} = \frac{1}{n} \left( E_{\text{tot}}^{M:H} - E_{\text{tot}}^{M} - \frac{n}{2} E(H_2) \right),$$

where  $E_{tot}^{M:H}$  is the total energy of the final configuration, containing *n* H atoms in the  $p(2 \times 2)$  unit cell (i.e., coverage  $\Theta = n/4$  ML),  $E_{tot}^{M}$  is the total energy of the initial clean metal surface, and  $E(H_2)$  is the total energy of the free H<sub>2</sub> molecule in the gas phase. Each configuration is described by its occupied sites within the  $p(2 \times 2)$  surface cell (h: hollow, b: bridge, t: top, o: octahedral subsurface site). In Table I we have compiled our results for several configurations between 0.25 and 2 mL. From these values one learns that at the lowest investigated coverage of 0.25 ML, the bridge site is lowest in energy. However, this is not completely true, since due to the high frequencies and the low mass of hydrogen, zero point corrections to the energy become crucial. By calculating the complete frequency spectrum of 3n modes  $\omega_i$  for the adsorbates in the  $p(2 \times 2)$  cell, we can calculate a zero point energy-corrected adsorption energy (for each isotope) with respect to the energy of the gas phase molecule  $E_0(H_2)$  (also including zero point energy)

$$E_{\text{ads}}^{H} = \frac{1}{n} \left( E_{\text{tot},0}^{M:H} - E_{\text{tot}}^{M} - \frac{n}{2} E_{0}(H_{2}) \right),$$
  
with  $E_{\text{tot},0}^{M:H} = E_{\text{tot}}^{M:H} + \frac{1}{2} \sum_{i=1}^{3n} \hbar \omega_{i}$ 

The corresponding values for deuterium are obtained using the by a factor of  $\sqrt{2}$  lower frequencies of the heavier isotope.

While in the hollow site all modes are rather low (88 meV perpendicular to the surface and 48 meV for the frustrated translation), frequencies for bridge adsorbed hydrogen are significantly higher (163 meV perpendicular to the surface and 125 and 32 meV for the frustrated translations; compare Table II). This leads to a difference in zero point energies for the two adsorption sites of 60 meV, which in turn favors the fourfold site. These zero point corrected adsorption energies are also compiled in Table I. In this table the adsorption energy per atom for the most favorable adsorbate configuration at a certain coverage is marked in bold. We find that up to a full monolayer the adsorption energy remains almost constant, and the hollow site is the favored adsorption position. The close energies of bridge and hollow sites are consistent with recent quantitative LEED studies of Klein et al.<sup>18</sup> for H on Rh(100), which have shown that their data could be described well only by assuming a mixture of hollow and bridge H atoms on the surface.

Going beyond 1 ML by adsorbing an additional H atom in a bridge site weakens the bond strength of the neighboring adsorbates, which are pushed by about 0.32 Å towards the bridge sites. This distortion costs energy, and hence the mean adsorption energy of configurations with less adsorbate– adsorbate repulsion (5b or 4h+t) is higher. This trend continues up to the highest investigate coverage of 2 ML.

In Fig. 11 the highest adsorption energies for each coverage are visualized. In this plot we have introduced another quantity,  $dE_{ads}$ , which takes into account the sequential character of the adsorption/desorption process. During adsorption a single molecule encounters a surface at a certain coverage, while the mean adsorption energy characterizes the configuration at a given coverage as a whole. Similarly, in TPD the desorption energy of a single molecule from the adsorbate covered surface is probed. This differential heat of adsorption  $dE_{ads}(\Theta)$  at coverage  $\Theta$  can be approximated via finite differences from our calculations of  $E_{ads}(\Theta)$ 

$$dE_{ads}(\Theta) = \frac{(\Theta + \delta\Theta)(E_{ads}(\Theta + \delta\Theta)) - (\Theta - \delta\Theta)(E_{ads}(\Theta - \delta\Theta))}{2\,\delta\Theta}$$

TABLE II. Calculated vibrations for different adsorption configurations (h:hollow sites, b: bridge, t: on top, o: octahedral, mol: molecular adsorbate) for hydrogen on Rh(100), divided into modes with eigenvectors predominantly perpendicular to the surface ( $\omega_{\perp}$ ) and such parallel ( $\omega_{\parallel}$ ). Frequencies for out-of-phase vibration (at the Brillouin zone boundary) are given in brackets to indicate the dispersion of the phonon band. At 1.25 and 1.5 ML the additional modes located mainly on the nonhollow adsorbed species are printed in bold face. In the case of a series of neighboring vibrational modes we have described them by a frequency range.

| Configuration (flat surface)   |                               |  |  |  |
|--------------------------------|-------------------------------|--|--|--|
| $(2 \times 2 \text{ cell})$    | $\omega_{\perp}$ (meV)        | $\omega_{\parallel}$ (meV)                       |  |  |
| 0.25 ML in hollow (1h)         | 88                            | 48   |  |  |
| 1 ML in hollow (4h)            | 91(82)                        | 58(65)   |  |  |
| 0.25 ML in bridge (1b)         | 163                           | 125, 32  |  |  |
| 1 ML in bridge (4b)            | 169(164)                      | 123 (110), 36(61)                                |  |  |
| 2 ML in bridge (8b)            | 173(167)                      | 153(132), 78(91,61)                              |  |  |
| 1.25 ML (4h+b.)                | <b>159</b> , 137(130), 88(85) | <b>103</b> , 92(102), <b>72</b> , 63(68), 20(48) |  |  |
| 1.25 ML $(4h+t)$               | <b>255</b> , 92(87)           | <b>57</b> , 37(82)                               |  |  |
| 1.25 ML (4h+o)                 | <b>111</b> , 91(84)           | <b>75</b> , 58–73                                |  |  |
| 1.50 ML (4h+20.)               | <b>104</b> , 88(81)           | <b>96</b> , 33–81                                |  |  |
| 1.50 ML (4h+mol.)              | <b>208</b> , 111(90)          | <b>305</b> , 43–74, <b>32(13)</b>                |  |  |
| Configuration metal adatom     |                               |  |  |  |
| $(2 \times 2 \text{ cell})$    |                               |  |  |  |
| One H atom on-top              | 236                           | 38   |  |  |
| Dimer on-top                   | 159                           | 365, 89  |  |  |
| 2 H on-top                     | 243                           | 22-48  |  |  |
| Configuration with metal dimer |                               |  |  |  |
| $(3 \times 3 \text{ cell})$    |                               |  |  |  |
| One atom bridging              | 171                           | 121, 47  |  |  |
| One atom on-top                | 236                           | 34   |  |  |

with  $\delta \Theta$ =0.125 ML. Analogously, this quantity can be calculated from the zero point corrected adsorption energies for H and D, yielding  $dE_{ads}^{H}$  and  $dE_{ads}^{D}$ , respectively. While this energy gain per incoming adsorbate is almost constant up to



FIG. 11. Average adsorption energies per atom ( $E_{ads}$ , and the respective zero point energy corrected values  $E_{ads}^{H}$  and  $E_{ads}^{D}$  for H and D) for the most favorite configurations calculated in a  $p(2 \times 2)$  cell for coverages varying between 0.25 and 2 ML (compare the bold face values in Table I). Additionally shown is the differential heat of adsorption  $dE_{ads}$ , determining the energy gain during adsorption at a given coverage (compare with the text).

1 ML, there is a pronounced drop around the measured molecular saturation coverage. This drop is related to the abovementioned adsorbate-adsorbate repulsion after all hollow sites have been occupied, and is even more pronounced for zero point corrected values. At even higher coverage (which is not accessible with molecular dosing) dE increases again, since the energy cost of destroying the 4 h structure was already paid at lower coverage. In the dE curves in Fig. 11 the isotope effect also can be traced nicely: while deuterium desorbs earlier up to 1 ML  $(dE_{ads}^{D} < dE_{ads}^{H})$ , the ordering changes for the higher coverage regime. In addition to surface species, we also investigated adsorption in subsurface sites. These positions are (up to a total coverage of 2 ML) less favored than surface species, but can be accessed via atomic adsorbates due to their high kinetic energies, as will be discussed later.

## **B. Vibrations**

For the calculation of the zero point energy a complete determination of the frequency spectra was necessary. Table II compiles some exemplary results. The frequencies at 0.25 ML were already mentioned before; both the frequencies for bridge and hollow adsorbed species agree with the findings of the present HREELS investigation and previous studies (Refs. 5 and 8 for hollow and Ref. 6 for bridge). With increasing coverage the frequencies shift up and in addition to that not only the gamma point but also the zone boundary becomes accessible by our calculations, and we get also information on the dispersion of the phonons. Both the upshift of the frequencies with increasing coverage and the width of the dispersion agree with the experimental results in Ref. 5. In the table we have also included some data for coadsorption structures based on a full ML of hollow adsorbed hydro

gen ( $\Theta$ =1.25 ML: 4h+b, 4h+t, 4h+o;  $\Theta$ =1.5 ML:4h +mol.). This has two effects on the spectrum: First, the additional adsorbate adds modes to the spectrum. On-top adsorption leads to the highest mode perpendicular to the surface (255 meV), followed by bridge (159 meV) and subsurface adsorption (114 meV). The last mode is in the expected frequency regime for subsurface adsorption [compare H on Ni(111) in Ref. 36]. The molecular species, adsorbed on top of a Rh atom, is characterized by the (slightly weakened) intramolecular mode around 305 meV and a frequency perpendicular to the surface of 208 meV. Second, the frequencies of the hollow adsorbed species become perturbed and broadened. Especially in the case of subsurface absorption, a slight buckling of the surface layer leads to a broad band ranging from 58 to 73 meV (33 to 81 meV) for one (two) subsurface hydrogen. Finally, in order to account for the roughening of the surface observed in the HREELS experiments, we investigated several configurations including Rh adatoms or dimers on top of the flat surface and calculated the corresponding frequencies for hydrogen adsorption.

## **VII. DISCUSSION**

The desorption spectra for hydrogen (deuterium) from Rh(100) exhibit two different desorption peaks, if molecular species are used for dosing (Fig. 1): A small peak located around 120 K ( $\alpha$  peak) and a dominant peak at 320 K ( $\beta_1$ peak), with a broad shoulder extending to 180 K. There is agreement in the literature that the  $\beta_1$  peak stems from recombinative desorption of H (D) atoms located in fourfold hollow sites.<sup>5</sup> The  $\alpha$  peak, which is only weakly pronounced in the case of dosing with molecular species, has been shown to increase significantly after postadsorption of CO.<sup>4,7</sup> We have demonstrated that we can induce a similar desorption peak without CO coadsorption, but by exposure to atomic deuterium only. This peak will be correlated with recombinative desorption of atoms via a molecular precursor state. In our experiments with atomic hydrogen and atomic deuterium exposure we can significantly populate a new desorption peak ( $\beta_2$ ) located around 170 K, which we attribute to desorption of subsurface species. In the following we will discuss the individual desorption peaks in detail and corroborate the conclusions with DFT calculations.

#### A. The $\beta_1$ -desorption peak

One essential prerequisite for the identification of individual desorption peaks is the quantitative determination of the coverage. In particular, for hydrogen and deuterium this is a tricky venture. Most of the techniques commonly used for this purpose (XPS,LEED) cannot be successfully applied in this case. Thermal desorption spectroscopy is a powerful method to detect hydrogen, but calibration of the spectra also requires a lot of precautions. Most often the saturation of a TD spectrum is arbitrarily chosen as 1 monolayer (ML), as also done for the hydrogen (deuterium)–Rh(100) case.<sup>8</sup> With our quantitative TDS,<sup>22</sup> however, we have obtained a saturation coverage of  $1.22\pm0.1$  ML, both for exposure with hydrogen and deuterium molecules. The series of hydrogen spectra with different exposure exhibits quite symmetric peaks up to 1 ML (thin dotted lines in Fig. 1), with peak maxima shifting from 360 K to 320 K with increasing coverage ( $\beta_1$  peak). This peak originates from the associative desorption of H (D) atoms located in hollow sites. This is corroborated by our HREELS investigations, which show a strong loss at 84 meV after saturation of the Rh(100) surface by using molecular hydrogen [Fig. 9, curve (a)]. This loss is in good agreement with literature data<sup>5</sup> and also with our calculated vibrational energies for H in fourfold hollow positions (see Table II).

A qualitative inspection of the  $\beta_1$  peak shape and the shift of the peak maxima indicates a second-order desorption reaction. Quantitative evaluation of the spectra using the methods by Parker, Jones, and Koel<sup>37</sup> or King<sup>38</sup> yields a desorption energy of 20 kcal/mol (870 meV/molecule) for small coverage, which decreases with increasing coverage. However, the pre-exponential factor also changes over several orders of magnitude. This is known as the "compensation effect," which has been described in detail in the literature.<sup>39-42</sup> The main message of this result is that in many cases the Polanyi-Wigner equation is just too simple to describe the desorption rate properly. A simulation of the desorption spectra according to the statistical mechanics model by Payne and Kreuzer,<sup>43</sup> using our calculated (coverage-independent) adsorption energies (Table I) and frequencies (Table II), as well as the experimentally obtained coverage dependence of the sticking coefficient, produced desorption spectra which fit quite well the experimental data in shape and peak position.

A peculiar feature of the  $\beta_1$  peak is the inverse kinetic isotope effect for the peak position: Deuterium desorbs at saturation at a temperature 8-10 K lower than hydrogen. This is a result of the different zero point energies for hydrogen and deuterium in the adsorbed phase and in the gas phase, as shown in Table I. It turns out that for the fourfold hollow sites the zero point energy does not depend strongly on the coverage. For example, between 0.25 and 1 ML the zero point energy per hydrogen (deuterium) atom changes from 100 to 104 meV (71 to 74 meV), respectively. For the free molecules the calculated zero point energies are  $E_0^{\rm H}(\text{free}) = 133 \text{ meV}$  and  $E_0^{\rm H}(\text{free}) = 94 \text{ meV}$  per atom, respectively. Since the adsorption potential well depth is the same for hydrogen and deuterium, the difference in the effective activation barrier for hydrogen and deuterium desorption is given by:  $\Delta E_{des} = E_0^{H}(\text{free}) - E_0^{H} - E_0^{D}(\text{free}) + E_0^{D}$ =  $E_{ads}^{H} - E_{ads}^{D}$  (see Table I). This yields an activation barrier for desorption at 1 ML which is about 9 meV/atom higher for hydrogen than for deuterium. This energy difference is about 2% of the calculated desorption energy for H and D in hollow sites (568 meV/atom, 559 meV/atom). Similarly, the  $\beta_1$ -peak shift in the desorption spectra of Fig. 1 (7 K) is also about 2% of the mean desorption temperature of 320 K.

### B. The $\beta_2$ -desorption peak

Above 1 ML, the additionally adsorbed hydrogen (for molecular dosing) desorbs in the lower temperature range of 100–280 K, in the form of a rather sharp peak at 120 K ( $\alpha$  peak) and a small, broad peak around 200 K. Up to about 0.25 ML can be contained in these states. However, by dos-

ing with hydrogen or deuterium in atomic form one can increase the population of these low temperature peaks significantly. The characteristics of this type of exposure is twofold: First, it is well known that exposure with hydrogen or deuterium in atomic form can lead to the population of subsurface sites.<sup>36,44–47</sup> This is due to the fact that possible activation barriers existing between surface sites and subsurface sites can be more easily overcome by impinging atoms because of the high initial potential energy of half of the dissociation energy (2.25 eV/atom). The same argument also holds for the population of additional adsorption sites on the surface, which also could not be occupied due to a possible high activation barrier for dissociation. Second, impinging atoms may react with adsorbed atoms in the form of Eley-Rideal reactions, hot atom abstraction reactions, or collision induced desorption reactions.<sup>26</sup> This can be utilized to remove selectively adsorbed species from the surface only, without influencing the absorbed species in subsurface sites significantly. The desorption spectra following atomic hydrogen exposure (Fig. 2) clearly show the growth of an extra peak, labeled  $\beta_2$ , in addition to the  $\beta_1$  peak. The maximum coverage  $(\beta_1 + \beta_2)$ obtained after exposure of  $8 \times 10^{18}$  H-atoms/cm<sup>2</sup> is 3.4 monolayers. A similar behavior is observed for atomic deuterium dosing. The additional sharp extra peak ( $\alpha$  peak) which appears in this case will be discussed later. From the coverage-exposure curve (Fig. 3) one can assume that even more than 3.4 ML hydrogen and deuterium can be accumulated on (in) the Rh(100) sample. This is a good indication that the  $\beta_2$  state stems from the recombination of hydrogen (deuterium) initially located in subsurface sites. The coadsorption (abstraction) experiments as shown in Fig. 5 and Fig. 7 confirm these assumptions. Impinging D atoms on a Rh(100) surface initially covered with 2.3 ML hydrogen remove hydrogen preferentially from the  $\beta_1$  state [Fig. 5(a)]. Note that the emptied sites are immediately refilled by impinging D atoms; therefore, the coverage of the  $\beta_1$  state is always close to 1 ML. Of course, some D atoms penetrate into the surface, contributing to a slight increase of the total coverage in the  $\beta_2$  state. Upon extended D exposure hydrogen is finally also removed from the  $\beta_2$  state, probably due to some site exchange between subsurface sites and temporarily empty surface sites during the impingement of atomic species or by a hot atom mechanism via subsurface H atoms. In Fig. 6 it is demonstrated that the removal of surface hydrogen  $(\beta_1)$  is very fast, whereas the removal rate of H from subsurface sites ( $\beta_2$ ) is smaller by a factor of 100.

Further inspection of Figs. 5(b), 5(c) shows that the  $\beta_2$  peak for H<sub>2</sub> has a rather long tail towards higher temperatures. This is an indication that the  $\beta_2$  desorption is diffusion limited. Apparently the subsurface species are not only located close beneath the surface, but are also distributed in deeper layers. This assumption is supported by the observed differences in the  $\beta_2$ -peak maxima as function of the dosing sequence with H and D. If the surface is first dosed with H and then with D, the  $\beta_2$  peak for deuterium starts at lower temperature than for hydrogen in the  $\beta_2$  state [Figs. 5(b), 5(c)]. In the case of impinging H atoms on a previously D-covered surface this behavior is reversed [Figs. 7(a)–



FIG. 12. Energy-path diagram describing the adsorption of hydrogen molecules and atoms on a precovered Rh(100) surface. The initial configuration (1/2 free  $H_2$ +0.75 ML or 1.0 ML on surface) defines the zero point of the energy scale. The change of the energy as function of the reaction coordinate is shown as a thick (0.75 ML) and thin line (1 ML precoverage). In the subsurface region, the larger energy wells correspond to octahedral interstitial sites of the first and second subsurface layers; the small minima in between correspond to tetrahedral subsurface sites.

7(c)]; hydrogen desorbs at somewhat lower temperature than deuterium in the  $\beta_2$  state. These results suggest that impinging atoms might actually force already adsorbed or absorbed atoms into deeper sites. A similar behavior of this "stamping" has already been observed in the case of H (D) adsorption on Pd(100).<sup>48,49</sup>

We have performed DFT calculations for the potential energies of a number of adsorption configurations and transition state configurations, to get a better understanding of the energies needed to move an atom from a surface site into a subsurface site. In Fig. 12 we show the calculated potential energy for a H atom as a function of the reaction coordinate from a surface site into an octahedral subsurface site for two different scenarios: Starting with four atoms in hollow sites (4h) the removal of a H atom into an octahedral subsurface site (final situation: 3h+1o) requires an activation energy of about 1.16 eV. The energy difference between the final and the initial state is 0.78 eV. For the transfer of a bridge hydrogen from the otherwise saturated surface (4h+1b) into the subsurface site (4h+1o), an activation barrier of 0.58 eV has to be surmounted. The energy difference between initial and final state is 0.20 eV. The activation barrier which has to be overcome to move an atom from an octahedral subsurface site into the octahedral site of the next layer underneath is 0.42 eV. These energies can be easily raised by the kinetic energy of the impinging atoms in the interaction region, which is about half of the dissociation energy (2.25 eV/atom)plus the initial kinetic energy according to the temperature of the hot doser (2000 K,  $E_{kin} = 2kT = 0.34 \text{ eV/molecule}$ ). The hydrogen atom in the octahedral site is located in a potential well which is 0.22 eV above zero with respect to the energy of  $\frac{1}{2}$  H<sub>2</sub> molecule in the gas phase (endothermic heat of solution). However, this metastable state is confined in this site by activation barriers of the order of 0.3-0.4 eV, and therefore stable at low temperatures. The calculated heat of solution (0.22 eV) is in reasonable agreement with the literature value of 0.28 eV.50

Exposure to atomic H (or D) results further in a pronounced roughening of the Rh(100) surface, as indicated by the reduction of the intensity of the elastic peak in HREELS by one order of magnitude (see Fig. 9, inset). Interestingly, this roughening does not influence the  $\beta_1$  desorption peak upon atomic exposure, as one can see by comparison of Fig. 1 and Fig. 2. The result of the surface roughening, however, is a decrease of the dipole scattering intensity in the HREELS experiment. This is caused by two different effects: (i) the specular scattering direction is quenched leading to spatially diffuse scattering, as indicated by the observed broad angular distribution of the primary peak, and (ii) the so-called surface selection rule reduces on a rough surface, on average, the perpendicular components of the dynamic dipole moments. In off-specular scattering geometry the impact scattering mechanism dominates over the dipole scattering mechanism,<sup>51</sup> and the dipole excited vibrations become suppressed relative to the nondipole processes in the loss spectra. This suggests that the loss spectra of Figs. 9(b) and 9(c) are dominated by nondipole processes. This loss of dipolar intensity may be responsible for the fact that the H-induced loss feature at 84 meV is not clearly visible in the spectra of the atomic H-exposed Rh(100) surface. The broad tail of loss intensities up to  $\sim 170$  meV loss energies indicates that a broad distribution of dipole and nondipole allowed vibrations from many inequivalent H adsorption sites contributes to this spectral region. Table II shows that many vibrations of H in hollow- and bridge-type Rh sites are possible in the region from  $\sim$  30–170 meV. Moreover, overtones of H vibrations, which have been observed by Richter *et al.*<sup>5</sup> for H on the flat Rh(111) surface, are likely to become more prominent on the roughened surface, contributing to the high energy end of the loss tail [see the broad feature between  $\sim$ 120–160 meV, Fig. 9, curve (b) and Fig. 10(A)].

A comparison of the temperature behavior of the loss spectra (Fig. 10) with the corresponding desorption spectra (Figs. 2 and 4) suggests that the loss intensity from  $\sim 30-170$  meV may be related to some extent with the  $\beta_2$  hydrogen (deuterium) state. An explicit association with particular subsurface H (D) sites is however difficult. The DFT calculations have found a range of vibrational frequencies from  $\sim 30-111$  meV as a result of H in octahedral subsurface sites below a H-saturated surface (see Table II). This is well within the range of the significant loss intensities experimentally observed. It has to be noted that the vibrations of subsurface H species are generally very weak in HREELS experiments due to the screening of the surrounding metal atoms and thus are difficult to detect.<sup>36,52,53</sup>

The loss peak at 202 meV on the atomic H saturated Rh(100) surface has a corresponding loss at ~150 meV on the atomic D saturated surface and the close to  $\sqrt{2}$  ratio of the two loss energies confirms its assignment as H (D) derived. The calculated vibrational modes in Table II give no clear indication on the origin of this loss, but some guidance may be obtained from the tabulated experimental frequencies of metal hydride coordination compounds.<sup>54</sup> In transition metal complexes metal (Ru,Rh,Pt)–hydrogen stretching vibrations have been observed as low as 200 meV for dihydrides, while the stretching vibrations in monohydrides occur at higher frequencies. On the roughened Rh(100) surface individual low-coordinated Rh adatoms may be in a similar situation as



FIG. 13. Energy-path diagram for adsorption of an  $H_2$  ( $D_2$ ) molecule on an Rh(100) surface, precovered with 1.0 ML of hydrogen (4h-config.).

in metal coordination complexes, and we suggest that the loss feature at  $\sim 200$  meV is due to Rh–hydride vibrations of particular low-coordinated Rh(H)<sub>2</sub> units.

## C. The $\alpha$ -desorption peak

The most interesting feature for exposure with atomic species is the strong development of the  $\alpha$ -desorption peak around 120 K for deuterium. On the other hand, a corresponding hydrogen peak does not show up for atomic hydrogen exposure, although a small peak exists upon *molecular* exposure in this temperature range. Some information concerning the nature of this peak can again be obtained from coadsorption experiments. In Fig. 5(d) we see that after sufficient exposure of an initially hydrogen covered surface (2.3 ML) with atomic deuterium the  $\alpha$  peak appears. But, whereas both the  $\beta_1$  peak and the  $\beta_2$  peak show at least some isotopic mixing into  $H_2$ , HD, and  $D_2$ , the  $\alpha$  peak is a pure D<sub>2</sub> peak. If the equivalent experiment is performed with reversed isotopes (H impinging on a surface covered with 2 ML of deuterium), the  $\alpha$  peak is quickly attenuated at the very beginning of H exposure |Fig. 7(a)|. These data clearly indicate that the  $\alpha$  peak stems from a surface species. The peculiar desorption behavior of the  $\alpha$  state (phenomenologically close to zero order desorption), however, indicates that desorption does not take place in form of a simple singlestep recombination reaction.

To support these assumptions we have performed DFT calculations of the reaction path from the initial free molecule above a hydrogen-covered surface (1 ML in fourfold hollow sites) into the final, dissociatively adsorbed state (see Fig. 13). The final state is characterized by two hydrogen atoms on top in addition to the four H atoms in hollow sites, which has been found to be one of the energetically most favorable configuration for the coverage of 1.5 ML. In the case of molecular dosing activation barriers have to be overcome for dissociative adsorption, which are inhibiting adsorption of thermal molecules. However, with atomic H (D) these adsorption sites can be easily populated. From the onedimensional potential energy diagram (Fig. 13) one can deduce that the rate of recombinative desorption of H atoms will be significantly influenced by the molecular precursor state. The population in the precursor state will always be high during desorption, and the desorption spectra will resemble a coverage-independent desorption (zero order desorption). The calculations are also in agreement with the observed isotope effect for the  $\alpha$  state in the saturated H<sub>2</sub> and D<sub>2</sub> desorption spectra (Fig. 1). Due to different zero point energies in the molecular state and the transition state, the effective activation barriers for desorption from the molecular state are 98 meV/molecule for hydrogen and 119 meV/ atom for deuterium, respectively.

In the case of molecular dosing only a small population of the  $\alpha$  state can be attained (~0.05 ML) due to the calculated high activation barriers for adsorption of about 130 meV/molecule for hydrogen and 116 meV/molecule for deuterium, respectively (zero point energy corrected). By using *atomic species* for dosing, no activation barrier has to be overcome and a much higher coverage of about 0.6 ML can be achieved. At sufficiently low adsorption temperature the "saturation" coverage could even be higher. Actually, desorption of molecularly adsorbed hydrogen in the temperature range 70–130 K has indeed been observed in some instances, particularly for stepped surfaces [Pd(210),<sup>55</sup> Ni(510)<sup>56</sup>].

The question of course now arises why the pronounced  $\alpha$  peak only appears for atomic deuterium exposure, but not for atomic hydrogen exposure. This is most probably correlated to the specific type of exposure. If atoms impinge on a surface, not only adsorption but also abstraction takes place simultaneously. The equilibrium coverage in the case of atomic exposure depends on the cross section for abstraction. Typically, for atomic hydrogen exposure on metal surfaces with adsorption energies of about 1 eV/molecule, the abstraction probability is much smaller than the sticking probability at empty sites, and therefore the equilibrium coverage is always close to saturation.<sup>26</sup> In the case of the weakly bound  $\alpha$  state and a possible high cross section for abstraction, the equilibrium coverage for this state will be much smaller than saturation.<sup>57,58</sup> In addition to that, the cross section is typically isotope dependent, in particular if hot-atom abstraction is the dominant process.<sup>59,60</sup> In such a case the incoming atoms are temporarily trapped in the surface potential well by converting sufficient normal energy into parallel energy. A hot atom can react with an adsorbed atom, and the reaction product (molecule) will immediately desorb from the surface, even at low temperature, due to the excess energy stored in the hot atom. The diffusion length for a hot hydrogen atom might be larger than for a deuterium atom, due to its smaller mass. In the case of the weakly bound  $\alpha$ hydrogen the removal by hot-atom abstraction is apparently so fast that no net uptake of hydrogen can take place.

## **VIII. SUMMARY**

Quantitative thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations have been applied to investigate the adsorption of hydrogen and deuterium on Rh(100). By using hydrogen (deuterium) in atomic form, one can populate adsorption sites which are not attainable with these species in molecular form. The results can be summarized as follows:

- (a) Exposure of the Rh(100) surface to molecular hydrogen or deuterium leads to dissociative adsorption mainly in fourfold hollow sites. Desorption from these sites proceeds around 300 K with a second-order-like desorption characteristic ( $\beta_1$  peak). The maximum coverage of 1.22 ML, as obtained by molecular dosing, hints at some additional population of other sites. Hydrogen adsorption in fourfold hollow sites is characterized by a vibrational loss energy of 84 meV.
- (b) Exposure of Rh(100) to atomic hydrogen (deuterium) leads to a pronounced roughening of the surface as evidenced by the HREELS experiments and to the strong population of the β<sub>2</sub> peak in TDS. The maximum coverage (β<sub>1</sub>+β<sub>2</sub>) obtained is 3.4 ML. By coad-sorption of H and D and thereby selective abstraction of surface species only, we can identify the β<sub>2</sub> peak as being the result of surface recombination of subsurface species.
- (c) The HREELS spectra of the atomic H (D) exposed surfaces are distinguished by nondipole excited processes on the rough surfaces, which lead to a broad region of enhanced loss intensity but without pronounced loss peaks. It is suggested that this is the result of many different inequivalent adsorption sites. A loss peak at  $\sim$ 200 meV ( $\sim$ 150 meV for D) is discussed in terms of a metal–dihydride-like stretching vibration of undercoordinated Rh(H)<sub>2</sub> units on the rough Rh(100) surface.
- (d) Exposure of Rh(100) to atomic deuterium leads, in addition to the population of subsurface sites, to an extra sharp desorption peak (α-peak) at about 120 K. This peak exhibits close to zero order desorption kinetics. By coadsorption/abstraction experiments we have identified this peak as being due to recombination of surface species. DFT calculations have shown that these species desorb via a molecular precursor state. The reason that this peak cannot be observed for hydrogen is possibly linked to the larger cross section for abstraction during atomic H dosing, compared to atomic D dosing.

## ACKNOWLEDGMENTS

This work has been supported by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung," within the joint research project: *Gas–Surface Interactions: Electronic Structure, Dynamics and Reactivity*, Project Nos. S8102, S8104, and S8106. We gladly acknowledge the supply of the Rh-crystal by P. Varga, Project No. S8103.

- <sup>1</sup>D. G. Castner, B. A. Sexton, and G. A. Somorjai, Surf. Sci. **71**, 519 (1978).
- <sup>2</sup>J. T. Yates, P. A. Thiel, and W. H. Weinberg, Surf. Sci. 84, 427 (1979).
- <sup>3</sup>D. E. Peebles, H. C. Peebles, and J. M. White, Surf. Sci. **136**, 463 (1984).
- <sup>4</sup>Y. Kim, H. C. Peebles, and J. M. White, Surf. Sci. 114, 363 (1982).
- <sup>5</sup>L. J. Richter, T. A. Germer, J. P. Sethna, and W. Ho, Phys. Rev. B **38**, 10403 (1988).
- <sup>6</sup>L. J. Richter, T. A. Germer, and W. Ho, Surf. Sci. **195**, L182 (1988).
- <sup>7</sup>L. J. Richter, B. A. Gurney, and W. Ho, J. Chem. Phys. 86, 477 (1987).
- <sup>8</sup>L. J. Richter and W. Ho, J. Vac. Sci. Technol. A 5, 453 (1987).
- <sup>9</sup>W. G. Durrer, J. H. Craig, and J. Lozano, Appl. Surf. Sci. 45, 275 (1990).

- <sup>10</sup>A. Eichler, J. Hafner, and G. Kresse, J. Phys.: Condens. Matter 8, 7659 (1996).
- <sup>11</sup>A. Eichler, G. Kresse, and J. Hafner, Surf. Sci. 397, 116 (1998).
- <sup>12</sup>A. Eichler, G. Kresse, and J. Hafner, Phys. Rev. Lett. 77, 1119 (1996).
- <sup>13</sup> A. Eichler, J. Hafner, A. Groß, and M. Scheffler, Phys. Rev. B **59**, 13297 (1999).
- <sup>14</sup>D. Hennig, S. Wilke, R. Löber, and M. Methfessel, Surf. Sci. 287/288, 89 (1993).
- <sup>15</sup>S. Wilke, D. Hennig, and R. Löber, Phys. Rev. B 50, 2548 (1994).
- <sup>16</sup>Y. Fukai, *The Metal-Hydrogen System* (Springer, Berlin, Heidelberg, 1993).
- <sup>17</sup> F. A. Lewis and A. Aladjem, *Hydrogen in Metal Systems II* (Scitec, Switzerland, 2000).
- <sup>18</sup>C. Klein, A. Eichler, E. L. D. Hebenstreit, G. Pauer, R. Koller, A. Winkler, M. Schmid, and P. Varga, Phys. Rev. Lett. (to be published).
- <sup>19</sup>J. K. Fremery, J. Vac. Sci. Technol. A 3, 1715 (1985).
- <sup>20</sup>U. Bischler and E. Bertel, J. Vac. Sci. Technol. A **11**, 458 (1993).
- <sup>21</sup>C. Eibl, G. Lackner, and A. Winkler, J. Vac. Sci. Technol. A 16, 2979 (1998).
- <sup>22</sup>A. Winkler, J. Vac. Sci. Technol. A 5, 2430 (1987).
- <sup>23</sup>P. A. Thiel, J. T. Yates, and W. H. Weinberg, Surf. Sci. **90**, 121 (1979).
- <sup>24</sup> H. Pölzl, G. Strohmaier, and A. Winkler, J. Chem. Phys. **110**, 1154 (1999).
- <sup>25</sup>G. Eilmsteiner, W. Walkner, and A. Winkler, Surf. Sci. **352**, 263 (1996).
- <sup>26</sup>A. Winkler, Appl. Phys. A: Solids Surf. **67**, 637 (1998).
- <sup>27</sup> Th. Kammler, J. Lee, and J. Küppers, J. Chem. Phys. **106**, 7362 (1997).
- <sup>28</sup>D. V. Shalashilin, B. Jackson, and M. Persson, J. Chem. Phys. **110**, 11038 (1999).
- <sup>29</sup>J. Harris and B. Kasemo, Surf. Sci. Lett. **105**, L281 (1981).
- <sup>30</sup>G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- <sup>31</sup>G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
- 32 http://cms.mpi.univie.ac.at/vasp/
- <sup>33</sup>G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1998).
- <sup>34</sup> J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- <sup>35</sup>G. Mills, H. Jónsson, and G. K. Schenter, Surf. Sci. 324, 305 (1995).
- <sup>36</sup> A. D. Johnson, K. J. Maynard, S. P. Daley, Q. Y. Yang, and S. T. Ceyer, Phys. Rev. Lett. **67**, 927 (1991).
- <sup>37</sup>D. H. Parker, M. E. Jones, and B. E. Koel, Surf. Sci. 233, 65 (1990).

- <sup>38</sup>D. A. King, Surf. Sci. **47**, 384 (1975).
- <sup>39</sup>E. G. Seebauer, A. C. F. Kong, and L. D. Schmid, Surf. Sci. **193**, 417 (1988).
- <sup>40</sup>D. Menzel, in *Interactions on Metal Surfaces*, Topics in Applied Physics, edited by R. Gomer, **4**, 101 (Springer, Berlin, 1975).
- <sup>41</sup>W. Curtis Conner, Jr., J. Catal. **78**, 238 (1982).
- <sup>42</sup>J. V. Niemantsverdriet, K. Markert, and K. Wandelt, Appl. Surf. Sci. 31, 211 (1988).
- <sup>43</sup>S. H. Payne and H. J. Kreuzer, Surf. Sci. **205**, 153 (1988).
- <sup>44</sup>U. Bischler, P. Sandl, and E. Bertel, Phys. Rev. Lett. **70**, 3603 (1993).
- <sup>45</sup>T. Kammler and J. Küppers, J. Chem. Phys. 111, 8115 (1999).
- <sup>46</sup>H. Premm, H. Pölzl, and A. Winkler, Surf. Sci. Lett. **401**, 444 (1998).
- <sup>47</sup>G. Krenn, C. Eibl, W. Mauritsch, E. L. D. Hebenstreit, P. Varga, and A. Winkler, Surf. Sci. 445, 343 (2000).
- <sup>48</sup>H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, and T. Aruga, Surf. Sci. Lett. **411**, L849 (1998).
- <sup>49</sup>H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, and T. Aruga, Surf. Sci. **427**, 277 (1999).
- <sup>50</sup> Gase und Kohlenstoff in Metallen, edited by E. Fromm and E. Gebhard (Springer, Berlin, 1976).
- <sup>51</sup> H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).
- <sup>52</sup>H. Okuyama, T. Nakagawa, W. Siga, N. Takagi, M. Nishijima, and T. Aruga, J. Phys. Chem. B **103**, 7876 (1999).
- <sup>53</sup>D. Farias, P. Schilbe, M. Patting, and K. H. Rieder, J. Chem. Phys. **110**, 559 (1999).
- <sup>54</sup>G. Socrates, Infrared and Raman Characteristic Group Frequencies— Tables and Charts (Wiley, Chichester, 2001).
- <sup>55</sup>P. K. Schmidt, K. Christmann, G. Kresse, J. Hafner, M. Lischka, and A. Groß, Phys. Rev. Lett. 87, 096103 (2001).
- <sup>56</sup> A. S. Martensson, C. Nyberg, and S. Anderson, Phys. Rev. Lett. **57**, 2045 (1986).
- <sup>57</sup>B. Jackson and D. Lemoine, J. Chem. Phys. **114**, 474 (2001).
- <sup>58</sup>T. Zecho, A. Güttler, X. Sha, D. Lemoine, B. Jackson, and J. Küppers, Chem. Phys. Lett. **366**, 188 (2002).
- <sup>59</sup>M. Persson and B. Jackson, Chem. Phys. Lett. 237, 468 (1995).
- <sup>60</sup>T. Kammler, D. Kolovos-Vellianitis, and J. Küppers, Surf. Sci. 460, 91 (2000).