Rotational and vibrational population of D_2 desorbing from sulfur covered Pd(100)

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We report rovibrational populations of D_2 desorbing recombinatively from sulfur covered Pd(100). The palladium surface is poisoned with an ordered c(2 × 2) overlayer corresponding to a coverage of $\Theta_S \approx 0.5$ ML. Desorbing D_2 molecules are detected with (1+1') REMPI via various $B\ ^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ Lyman bands using tunable vacuum ultraviolet (VUV) laser radiation for the excitation step. Rotational quantum states $J'' = 0$ to 12 in the vibrational ground and $J'' = 0$ to 8 in the first vibrational excited state are measured. Experiments are performed for surface temperatures in the range from $T_S = 500 - 800$ K. Rotational energies lower and vibrational energies higher than the corresponding surface temperature are observed. The vibrational energies are higher than those of molecules desorbing from a clean Pd surface. The experimental results are compared with quantum dynamical calculations for the desorption of H_2 from a p(2 × 2) sulfur-covered Pd(100) surface, based on a potential energy surface (PES) derived from density functional calculations. While the observed rotational cooling for molecules in the vibrational ground state is reproduced by the calculations, the vibrational effects are underestimated.

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I. INTRODUCTION

The catalytic activity of surfaces is often significantly modified by the presence of co-adsorbates. Sulfur atoms act as inhibitors for surface reactions and therefore poison catalysts. An understanding of the microscopic mechanisms of surface reactions is developed through the investigation of model systems, like the associative desorption of hydrogen from metal surfaces. Experimentally the study of all molecular degrees of freedom – rotational and vibrational energy, internal state-specific velocity and angular distributions, and the influence of the spatial alignment of the rotational angular momentum – yields dynamical information about the reaction. In a addition to these quantities a theoretical treatment allows further to investigate the influence of the location within the surface unit cell on the reaction. At the clean palladium surface hydrogen reactions have extensively been studied[1,2] in the past both experimentally[3–10] and theoretically[11–19]. The potential energy surface for the reaction on a clean palladium surface shows a significant energetic and geometric corrugation. In particular, reaction paths without barrier as well as activated paths with barriers up to $E_b = 200$ meV are available[12,17,18]. This leads to a variety of interesting dynamical effects, like steering of molecules with low kinetic energy[11] and small angular momentum[17] to favorable adsorption sites. These calculations predict a significant rotational cooling of associatively desorbing hydrogen molecules, in good agreement with experimental results[10].

For the sulfur poisoned system only a few experimental data are available[3,6,20,21]. Recently a six-dimensional potential energy surfaces (PES) has been obtained using a density functional approach[22]. High-dimensional quantum calculations of the reaction dynamics on this PES have been performed[16,19]. These theoretical investigations of the sulfur poisoned palladium surface[22–24] predict an increase of the energetic barriers for the dissociative adsorption of hydrogen. At the p(2×2) S/Pd(100) surface the reaction shows a minimum barrier at the hollow and bridge sites of about $E_b = 110$ meV, and at the on-top site one of $E_b = 1.2$ eV . Calculations for the c(2 × 2) structure show that at thermal energies the hydrogen dissociative adsorption is always repulsive for all adsorption sites. At this surface the reaction at the hollow site shows a minimum barrier of about $E_b = 1.8$ eV and at the on-top site one of $E_b = 2.5$ eV is obtained. For the c(2 × 2) structure the barriers are thus much higher than for the p(2 × 2) sulfur overlayer[22]. For both structures non-activated reaction paths disappear completely by sulfur adlayers. In this paper we report experimental results on the population of internal states for molecules desorbing from the sulfur covered Pd(100) surface and compare these data with high-dimensional quantum dynamic calculations on the PES for the p(2 × 2) sulfur overlayer. The experimental investigations started with a well ordered c(2 × 2) sulfur overlayer which, however, decreases during an experimental run.

II. TECHNICAL DETAILS

A. Experimental method

The experiments are performed in an ultra-high vacuum chamber pumped by turbo molecular and titanium getter pumps to a base pressure of less than 2×10^{-10} mbar. Order and cleanliness of the surface are determined by low-energy electron diffraction (LEED) and Auger spectroscopy. Adsorbates are removed when necessary by soft Ar^+ ion sputtering at low energy and current density. After sputtering the surface is allowed to anneal before it is poisoned with sulfur. A well defined sulfur adlayer is produced by dosing the palladium surface with H_2S. After dosing LEED and Auger spectroscopy are employed to control the order of the adlayer and the amount of sulfur deposited. The sulfur coverage is determined from the Auger peak ratio of sulphur (151 eV) and palladium (330 eV) calibrated at the c(2×2) structure. Various preparations show Auger peak ratios of I_{151}/I_{330} between 0.65 and 0.75 from which we conclude that a ratio of 0.7 corresponds to a coverage of $\Theta_S = 0.5$ ML. Deuterium atoms are supplied to the surface of the crystal by atomic permeation through the bulk of the 1 mm thick sample. The sample is radiatively heated to temperatures between 500 K and 800 K. The investigation of the sulfur overlayer with LEED and Auger spectroscopy after each experimental run has shown that the amount of sulfur decreases during the desorption process. Auger spectroscopy reveals that the sulfur coverage decreases expontially in the first 12 minutes to about a quarter of a monolayer. This coverage then remains stable also for longer times. As shown by LEED the overlayer does not correspond to the p(2 × 2) structure, rather a c(2 × 2) structure is still observed, although with largely broadened spots.

Rotational state selective detection of desorbing molecules is performed by (1+1') REMPI. Deuterium molecules are electronically excited in the $B\ ^1\Sigma_u^+(v', J') \leftarrow X\ ^1\Sigma_g^+(v'', J'')$ Lyman system with vacuum ultraviolet (VUV) laser radiation tunable in the $\lambda = 106 - 110$ nm spectral range. The VUV radiation is generated by frequency tripling the second harmonic of tunable dye laser radiation in krypton and xenon. Rovibrational states in the Lyman (0-0) to (3-0) and (3-1) to (5-1) bands are detected. A second UV photon at $\lambda = 266$ nm ionizes the excited molecules. The excitation photons and the ionization photons are both linearly polarized parallel to the surface normal. The photoions produced are detected by microchannel plates (MCP). In order to derive rovibrational populations of the electronic ground state the transition rates for both the excitation and the ionization step have to be known. The transition probabilities for the ionization step strongly vary for different rovibrational (v', J') levels of the intermediate B state[25,26]. We therefore determine relative ionization probabilities by observing, at the given laser intensities, the ion yield of D_2 leaving a Knudsen cell with a fixed temperature and thus a well-known Boltzmann state distribution. A detailed description of this calibration has been given previously[10]. Rotational state populations could be determined for D_2 ($J'' = 0 - 12$) in vibrational ground and D_2 ($J'' = 0 - 8$) in the first vibrational excited state.

Molecules desorbing from the palladium surface are detected at a distance of 20 mm from the surface. Since the experiments are carried out with a continuous desorption flux, some molecules may reach the detection volume after having thermally equilibrated at the chamber walls. This background is partly suppressed by separating the desorption chamber containing the Pd sample from the detection volume, and allowing only the central part of the desorption flux to enter the detection chamber through a 10 mm diameter aperture. The residual background gas is accounted for by taking spectra of the background gas only. Due to its thermal population at $T \sim 300$ K this background has a noticeable influence only on the ion signal for molecules in $J'' = 0$ to 5 in the vibrational ground state. The ion signal I observed is then connected to the rovibrational state population $N(v'', J'')$ via

$$I \propto \left|R_e^{n'n''}\right|^2 \left|R_{\text{vib}}^{v'v''}\right|^2 S_{J'J''}\, K(v', J')\, \chi(v'', J'')\, N(v'', J''). \tag{1}$$

Here, $\left|R_e^{n'n''}\right|^2$ and $\left|R_{\text{vib}}^{v'v''}\right|^2$ denote the electronic transition moment and the Franck-Condon factor, respectively, and $S_{J'J''}$ describes the Hönl-London factor. $K(v', J')$ takes the relative detection sensitivity as determined above into account. The influence of the rotational alignment of desorbing molecules is described by the polarization factor $\chi(v'', J'')$. This factor compensates for the dependence of the excitation probability on the angle between the transition moment and the polarization of the exciting laser. The alignment of $D_2(v'', J'')$ desorbing from c(2 × 2) / Pd(100) has recently been determined in this laboratory[21].

B. Theory

The theoretical background of the calculations has been described in detail in Ref. 27. Here we only recall some fundamentals. The interaction potential of hydrogen with the sulfur-covered Pd(100) surface has been determined by density-functional theory (DFT) calculations in the generalized gradient approximation[22]. These *ab initio* results have been parametrized for the p(2×2) sulfur-covered Pd(100) surface by an analytical expression to yield a continuous potential energy surface (PES)[22]. This PES has been used in quantum mechanical coupled-channel calculations[28], in which all six hydrogen degrees of freedom were explicitly taken into account; the substrate, however, was kept fixed. This is a reasonable approximation considering the large mass mismatch between hydrogen and palladium.

In the quantum mechanical simulations state-specific sticking probabilities $S_n(E_\perp)$ as a function of the incident normal kinetic energy $E_\perp$ are determined. Here n stands for a multi-index that describes the initial vibrational, rotational and parallel momentum state of the molecule. From these sticking probabilities vibrational and rotational distributions in desorption are derived via the principle of detailed balance or microscopic reversibility[29]. In detail, the population N_n of the state n in desorption at a surface temperature of T_s is given by

$$N_n(E_\perp) = \frac{1}{Z}\, S_n(E_\perp) \exp\left[-(E_n + E_\perp)/k_B T_s\right]. \quad (2)$$

Here $E_\perp$ is the kinetic energy perpendicular to the surface, E_n is the energy associated with the internal state N, and Z is the partition sum that ensures the normalization of the distribution. To obtain the mean vibrational and rotational energies in desorption, the appropriate average over the probabilities N_n has to be performed. Since the substrate is kept fixed in the simulation, it does not participate dynamically in the adsorption/desorption process. Still it is assumed to act as a heat bath that determines the population distribution of the molecular states in desorption.

The rather large surface unit cell of the p(2×2) sulfur-covered Pd(100) surface requires the use of a large basis set in the expansion of the hydrogen wave function which causes a significant computational effort for the quantum coupled-channel calculations. Therefore the quantum dynamical reaction probabilities have only be calculated for the sub-manifold of even rotational and azimuthal quantum numbers J and m_J. Thus in the partition sum also only rotational states with even quantum numbers J and m_J are included. The error associated with this reduced subset of rotational states for the rotational and vibrational temperature in desorption has been estimated to be below 2%.

III. RESULTS AND DISCUSSION

A. Rotational state distribution

Rotational state populations for D_2 desorbing from a sulfur covered Pd(100) surface at $T = 745\,\mathrm{K}$ are shown in Fig. 1 for both vibrational states $v'' = 0$ and $v'' = 1$, indicated by filled squares and opened circles, respectively. The population data displayed in Fig. 1 are averaged over P- and R-branch measurements. The ortho- and para-D_2 fit to common curves, implying that they are populated statistically. For an ensemble in thermal equilibrium a Boltzmann plot as shown in Fig. 1 should exhibit a linear dependence with a slope of $(-1/k_B T_{\mathrm{rot}})$. As is evident, the rotational state population data of the vibrational ground state do not resemble a Boltzmann distribution. The overpopulation at low ($J'' = 0$ to 2) and high ($J'' = 10$ to 12) rotational states can clearly be discerned. It is possible to fit the population distribution by two Boltzmann temperatures of $T_1 = 388\,\mathrm{K}$ and $T_2 = 1118\,\mathrm{K}$. This composed fit reveals a strong rotational cooling effect for D_2 in low-J'' states, while the higher J'' are rotationally heated to a considerable extent. Similar distributions are observed at all surface temperatures investigated.

To account for the non-Boltzmann behavior of the rotational population distribution the average rotational energy $\langle E_{\mathrm{rot}}\rangle = \sum_{J''} N(v'', J'') E_{\mathrm{rot}}(J'')$ is calculated. For a consistent assessment of the rotational energy the population in rotational states $J'' = 0$ to 12 is used in both vibrational states $v'' = 0$ and 1. In cases the experimental sensitivity did not permit to measure a state population directly its value is taken from a fit of the measured data to the two rotational temperatures, as described above. At $T_S = 745\,\mathrm{K}$ the rotational energy in the vibrational ground state amounts to $\langle E_{\mathrm{rot}}\rangle = 438\,\mathrm{cm}^{-1}$, and for the vibrational excited state we obtain $\langle E_{\mathrm{rot}}\rangle = 608\,\mathrm{cm}^{-1}$. The resulting rotational temperatures of $T_{\mathrm{rot}} = 630\,\mathrm{K}$ and $T_{\mathrm{rot}} = 875\,\mathrm{K}$ for $v'' = 0$ and 1, respectively, are plotted in figure 2.

The average rotational energies measured at different surface temperatures are shown in figure 2. The data obtained for molecules desorbing in the vibrational ground and the first vibrationally excited state are shown as filled squares and open circles, respectively. The full line represents the line of complete accommodation to the surface temperature T_S. Molecules desorbing in the vibrational ground state possess a lower rotational energy than expected for molecules equilibrated at the surface temperature. Molecules in the vibrationally excited state show a rotational energy higher than expected from the surface temperature. Rotational temperatures previously obtained for D_2 molecules desorbing in the vibrational ground state from clean Pd(100)[10] are very similar to the present results measured for the S/Pd(100) surface. Theoretical rotational temperatures calculated for the p(2 × 2) S/Pd(100) surface are also shown in this figure. The dashed and dotted lines represent the results obtained for $v'' = 0$ and 1, respectively. For both vibrational states a slight rotational cooling is thus theoretically expected, while a significantly more pronounced cooling is experimentally measured for the ground state. For molecules desorbing in $v'' = 1$ theoretically a stronger cooling is expected than for $v'' = 0$, while experimentally even a rotational heating is observed. For the clean surface on the other hand a good agreement between the experimental and theoretical results has been obtained[10].

One should note, however, that in the present study theory and experiment have investigated different surface systems. The experimental investigations started with a well-ordered, half a monolayer coverage of sulfur in a c(2 × 2) structure, which decreased during an experimental run to about a quarter of a monolayer. This sulfur adlayer does , however, not form a well-ordered p(2 × 2) structure, which is examined by the theoretical investigations. Furthermore, the calculations shown are performed for H_2 while the experiments have been carried out with D_2.

As is exemplified in figure 1, molecules with low rotational states have a greater desorption probability than thermal molecules. With increasing J'' this probability decreases to a minimum at $J'' \approx 5$. With further increasing J'' the desorption probability increases again. The fraction of the measured population, $N_{\mathrm{exp}}(v'', J'')$, and a population corresponding to the surface temperature,

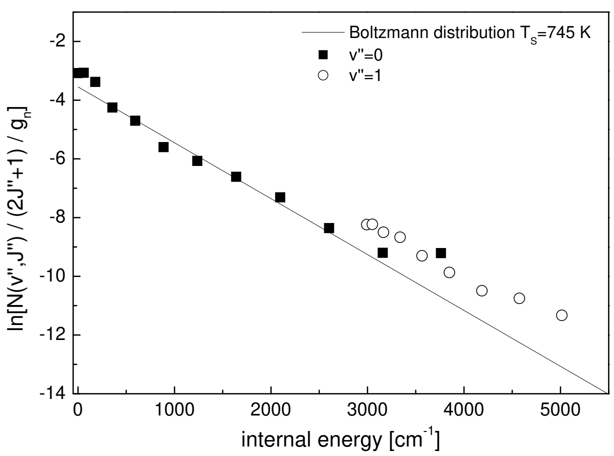

FIG. 1: Measured rovibrational population $N(v'', J'')$ for D_2 desorbing from S/Pd(100) at $T_S = 745\,\mathrm{K}$. Filled squares: $D_2(v'' = 0)$; open circles: $D_2(v'' = 1)$; line: population for $T_S = 745\,\mathrm{K}$.

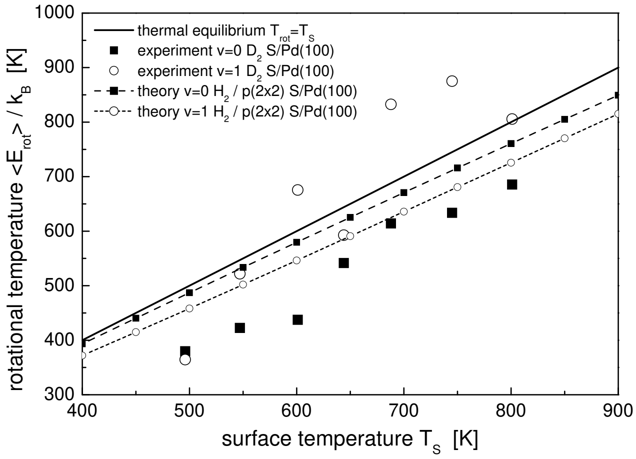

FIG. 2: Rotational energy E_{rot} plotted as $T_{\mathrm{rot}} = E_{\mathrm{rot}}/k_B$ versus the surface temperature T_S. Filled squares: $D_2(v'' = 0)$; open circles: $D_2(v'' = 1)$; solid line: thermal equilibrium with $T_{\mathrm{rot}} = T_S$. Theoretical results for $H_2(v'' = 0)$ (dashed line) and $H_2(v'' = 1)$ (dotted line) desorbing from the $p(2 \times 2)$ S/Pd(100) surface are also shown.

$N_{\mathrm{B}}(v'', J'', T_S)$, is proportional to the relative desorption probability. For molecules desorbing in the vibrational ground state the results are shown in a semi-logarithmic plot in figure 3. These results show first a decrease of the desorption probability up to $J'' = 5$ and then an increasing desorption probability. This behavior is the same for all experimental surface temperatures. The sticking probability for the reverse process of dissociative adsorption is measured by Gostein et al.[30] and calculated by Dino et al.[31] for the clean D_2/Pd(111) system. At this system both experimental and theoretical result show a decreasing of the sticking probability up to $J'' = 2$ to 4 and then an increasing sticking probability with increasing J''. This behavior for the desorption and the adsorption probability can be explained by two different reaction processes: the rotational steering[17] and rotational-translational energy transfer. The process of rotational steering is dominant for low rotational states. Molecules in low-J'' states, $J'' \leq 2$, can effectively be steered to an adsorption geometry within the surface unit cell which shows a low barrier for reaction. Similarly, molecules in high-J'' states, $J'' \geq 9$, have sufficient rotational energy to overcome after rotational-translational coupling any barrier in the dissociative adsorption potential on the $p(2 \times 2)$ S/Pd(100) surface. Their relative sticking probability is thus also high. Molecules in $J'' = 3$ to 7, however, can neither be effectively steered nor have sufficient rotational energy to overcome the barrier. Their sticking probability is therefore lower and in adsorption a significant fraction is reflected. In figure 3 is also shown the effect of vibrationally assisted sticking. Vibrationally excited molecules, $D_2(v'' = 1)$, have a greater desorption probability than thermal molecules and molecules in the vibrational ground state ($v'' = 0$). The J''-dependent sticking in $v'' = 1$ is similar to the behavior of the rotational degree of freedom in the ground state.

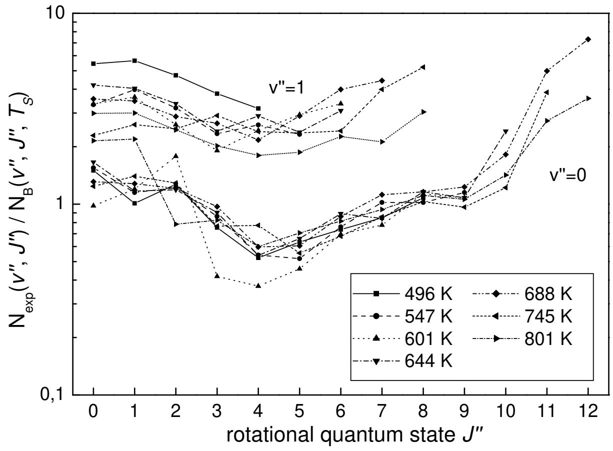

FIG. 3: $N_{\mathrm{exp}}/N_{\mathrm{B}}$ of $D_2(v'' = 0, 1)$ desorbing from S/Pd(100) as a function of the rotational quantum state J'' for different surface temperatures.

The rotational cooling is caused by the rotational steering effect. The majority of molecules are desorbing in rotational states with low quantum number and thus low rotational energy. The average rotational energy is then lower than expected for molecules in thermal equilibrium at T_S. Molecules desorbing in the first vibrational state have rotational energies on average larger than T_S. In this state rotational steering is thus not important to promote dissociative sticking. Rather, vibrationally assisted sticking[22] is the dominant mechanism to overcome the reaction barrier, see below. In addition in all rotational states of $v'' = 1$ rotational-translational energy transfer supports the reaction.

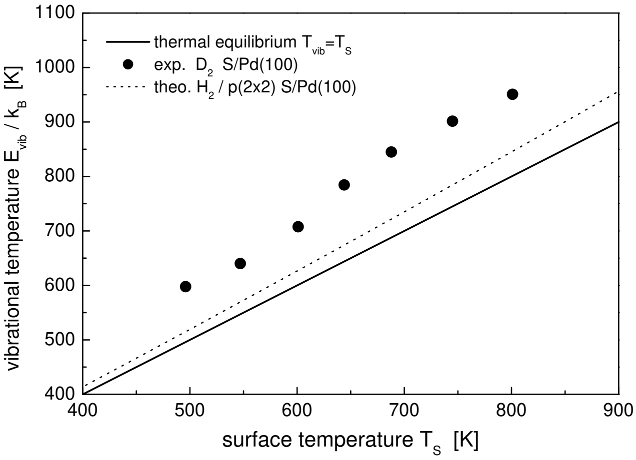

FIG. 4: Vibrational energy $E_{\rm vib}$ plotted as $T_{\rm vib} = E_{\rm vib}/k_B$ versus the surface temperature T_S. Filled circles: experimental results for the sulfur covered surface; dashed line: theoretical results for the H_2/ p(2×2) S/Pd(100) structure; solid line: thermal equilibrium with $T_{\rm vib} = T_S$.

B. Vibrational state distribution

The vibrational temperature is determined from the relative population in the two vibrational states investigated. Fig. 4 shows the measured vibrational temperatures for all surface temperatures studied as filled circles. The solid line represents again the line of full accommodation of the vibrational degree of freedom to the surface temperature. All experimental data show a temperature higher than the corresponding surface temperature. Obviously, an enhanced vibrational excitation occurs for recombinative D_2 desorption from the sulfur covered Pd(100) surface. The population of the $v'' = 1$ state is on average a factor of 3.0 higher than the corresponding thermal population.

In an earlier experiment[10] we studied the vibrational excitation of D_2 desorbing from a clean palladium surface. Also in this case an excess vibrational population was observed. The average overpopulation amounted to a factor of 1.76 compared to thermal equilibrium, thus lower than observed for the sulfur covered surface. For the clean surface the vibrational heating is caused adiabatically by the lowering of the hydrogen vibrational frequency upon dissociation[10,29,32,33]. This bond weakening has a stronger effect on the effective potential of the higher vibrational states than on the ground state leading to the vibrational heating. This mechanism is dominantly effective only when non-activated pathways for dissociative adsorption are available. For the sulfur poisoned palladium surfaces such non-activated reaction paths cease to exist. For S/Pd(100) the theoretical PES shows strong curvatures in the reaction path, however, with an early location of the barrier[22]. The strong curvature favors vibrational excitation in dissociative sticking while an early barrier reduces the vibrational efficacy. The theoretical values for the vibrational population obtained from the quantum dynamic calculations on the six-dimensional energy surface for H_2/ p(2×2) S/Pd(100) are shown by the dotted line in Fig. 4. This calculation also yield a vibrational heating, but less pronounced than experimentally observed. The dynamical situation is thus different from hydrogen adsorption on copper where a strong curvature of the PES and a late barrier strongly favors vibrational excitation[34,35], as was experimentally observed[36].

Again, we have to point out that the calculations are made for the p(2×2) structure whereas the experimental results are obtained for a surface with changing sulfur coverage. As already mentioned, the PES for H_2/c(2×2)S/Pd(100) has also been calculated. However, the calculated PES is almost purely repulsive with a minimum barrier for dissociation in the order of 2 eV. This would mean that hydrogen molecules desorbing from this surface should have a kinetic energy of about 2 eV, while experimentally a mean kinetic energy of $0.18 - 0.25$ eV has been observed[3]. The experimental situation, however, does not correspond to a well ordered c(2×2) structure so that associative desorption may be dominated by paths at sites with a locally lower sulfur coverage. While an error in the DFT calculations due to the uncertainty in the exchange-correlation functional cannot be excluded, an error of 2 eV seems to be unreasonably high. The scenario with the locally lower sulfur coverage dominating the desorption flux could give a consistent explanation for the deviation between theory and experiment. These sites will probably still have a higher barrier than at the p(2×2) S/Pd(100) structure, caused by the overall repulsive effect of sulfur, but they will not show barriers in the order of 2 eV. High barrier systems such as H_2/Cu usually show a high vibrational efficacy[1,2] leading to a significant vibrational heating in desorption. This would then explain why the observed vibrational heating of hydrogen desorbing from the S/Pd(100) surface is larger than the one calculated for desorption from the p(2×2)S/Pd(100) surface.

In Fig. 5 the vibrational heating is also shown in an Arrhenius analysis of the data , where the logarithm of the vibrational population is plotted versus the inverse surface temperature. From a least-squares fit of the measured data an activation energy of 310 meV is derived (straight line in Fig. 5). The free D_2 molecule shows an excitation energy for $v'' = 1$ of 371 meV. At the c(2×2) S/Pd(100) surface thus a reduction of the vibrational activation energy of D_2 occurs. This vibrational energy of the already stretched molecule is slightly lower than for dissociation at the clean surface, where a corresponding activation energy of 344 meV was observed[10].

IV. CONCLUSION

We have presented experimental results for the internal state-resolved desorption probability for D_2 from the

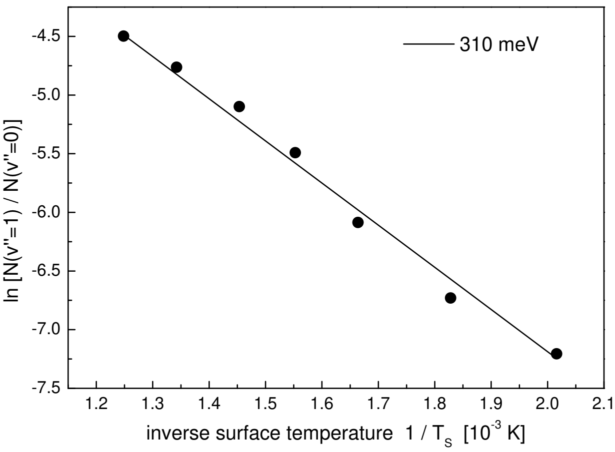

FIG. 5: Arrhenius plot of the relative population of D_2 ($v'' = 1$) as a function of inverse surface temperature T_S^{-1}. The straight line represents a least-squares fit to the data with an activation energy of 310 meV.

S/Pd(100) surface. In the vibrational ground state the average rotational energy of the desorbing molecules is lower than expected for molecules in thermal equilibrium with the Pd surface. Further, the low J''-states are more populated than expected for an equilibrium distribution. This rotational cooling can be explained via the principle of detailed balance by the rotational steering at low J'' and as the rotational hindering in adsorption for high-J'' due to the anisotropy of the underlying potential energy surface. The vibrational temperature in desorption, on the other hand, is significantly larger than expected for thermal equilibrium with the surface temperature and larger than the vibrational temperatures of D_2 desorbing from the clean Pd(100) surface. Theoretical quantum dynamic calculations based on a six-dimensional PES for the p(2×2) S/Pd(100) surface can currently not satisfactorily describe the experimental results for the reaction on S/Pd(100). Investigations of the sulfur coverage before and after a desorption experiment show a decreasing amount of sulfur which could be caused by desorption of D_2S. This damaging the well-ordered sulfur adlayer may only be effective in desorption experiments, where the adsorbed D atoms come closer to the sulfur atoms. In adsorption experiments thermal molecules with low kinetic energy do not reach the surface, because of the high repulsive potential barrier at the c(2×2) overlayer, molecules with high kinetic energies may, however, also react with adsorbed S atoms leading to a change of the coverage.

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