ELSEVIER

Surface Science 357–358 (1996) 614–618

surface science

# Six-dimensional quantum dynamics of adsorption and desorption of $H_2$ at Pd(100): no need for a molecular precursor adsorption state

Axel Gross *, Steffen Wilke, Matthias Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany*

Received 15 August 1995; accepted for publication 1 November 1995

**Abstract**

We report six-dimensional quantum dynamical calculations of dissociative adsorption and associative desorption of the system $H_2$/Pd(100) using an ab initio potential energy surface. We focus on rotational effects in the steering mechanism, which is responsible for the initial decrease of the sticking probability with kinetic energy. In addition, steric effects are briefly discussed.

*Keywords:* Atom–solid interactions, scattering, diffraction; Chemisorption; Density functional calculations; Hydrogen; Low index single crystal surfaces; Metallic surfaces; Models of surface chemical reactions; Molecule–solid reactions; Palladium; Quantum effects

## 1. Introduction

In recent years the dynamics of dissociative adsorption has been the subject of a large number of experimental and theoretical investigations (see, e.g. Refs. [1–4]). As far as quantum dynamical simulations were concerned, these studies were restricted to low-dimensional calculations on model potentials due to computational constraints and the non-availability of ab initio potential energy surfaces (PES). By varying potential parameters it was tried to reproduce experimental results qualitatively. These studies laid the foundations of the current understanding of simple surface reactions and of the topological features that realistic potentials should have. The main effects of molecular vibration [5–10], rotation [11–16] and lateral corrugation [17,18] on the dissociative adsorption probability seemed to be understood to a large extent, but it remained unclear whether the qualitative explanations would still be valid in high-dimensional dynamical calculations including all crucial degrees of freedom.

Just recently it has become possible to evaluate the six-dimensional potential energy surface of hydrogen dissociation on metal surfaces [19–22] by density-functional theory. This development also motivated new efforts for improving the quantum dynamical algorithms. Indeed it is now feasible to perform studies of hydrogen dissociation where *all* six degrees of freedom of the hydrogen molecule are treated quantum mechanically [23]. These calculations showed that the initial decrease of the sticking probability with kinetic energy found experimentally for $H_2$ on Pd(100) [24] and on many other transition

* Corresponding author. Fax: +49 30 8413 4701; e-mail: axel@theo22.rz-berlin.mpg.de.


*PII* S0039-6028(96)00232-4

metal surfaces [25–30] is not due to a precursor mechanism, as was commonly believed, but can be explained by dynamical steering.

In this contribution we will – after briefly recalling the theoretical background and the main result of our previous study [23] – focus on the influence of rotations on the adsorption dynamics in the system $H_2$/Pd(100). We will describe the dependence of the sticking probability on the initial rotational quantum number $j_i$ of the impinging hydrogen molecules and show how this dependence could be verified experimentally. We end with a brief discussion of steric effects and concluding remarks.

## 2. Theoretical background

The potential energy surface of $H_2$/Pd(100) has been determined using the density-functional theory together with the generalized gradient approximation (GGA) [31] and the full-potential linear augmented plane-wave method [32,33]. Ab initio total energies have been evaluated for more than 250 configurations and have been parametrized in a suitable form for the dynamical calculations [23]. The substrate atoms are assumed to be fixed since due to the large mass mismatch between adsorbate and substrate for $H_2$/Pd there is only little energy transfer to the substrate phonons. The quantum dynamics is determined in a coupled-channel scheme within the concept of the *local reflection matrix* (LORE) [34,35] and the *inverse local transmission matrix* (INTRA) [36]. This very stable method, which has been employed before in a high-dimensional study of the adsorption of $H_2$/Cu(111) [37], is closely related to the logarithmic derivative of the solution matrix and thus avoids exponentially increasing outgoing waves, which cause numerical instabilities. By utilizing all symmetries of the hydrogen wave function it has been possible to effectively include up to 21 000 channels per total energy in the dynamical calculations.

## 3. Results

Fig. 1 presents the results for the sticking probability as a function of the kinetic energy of the $H_2$ beam incident on a Pd(100) surface [23]. The dashed curve, which corresponds to $H_2$ molecules initially in the rotational ground state $j_i = 0$, exhibits a strong oscillatory structure for low energies. These oscillations are a consequence of the quantum nature of the hydrogen beam [18,38]. They are smoothed out if the initial rotational population and the energy spread typical for molecular beam experiments [24] are taken into account (solid line in Fig. 1). This curve should be compared with the experimental results of Rendulic et al. [24], which were obtained at a low surface temperature of 170 K. The theoretical curve agrees quite well with the experimental data. The still remaining discrepancies could be caused by, e.g. the influence of the thermal motion of the substrate atoms, by defects or impurities on the surface, or by uncertainties in the determination of the PES. However, more important is the general qualitative result, which is also relevant for other hydrogen on transition metal systems: although no precursor state exists in the PES and the energy transfer to substrate phonons is not taken into account, the initial decrease of the sticking probability with increasing kinetic energy is well reproduced.

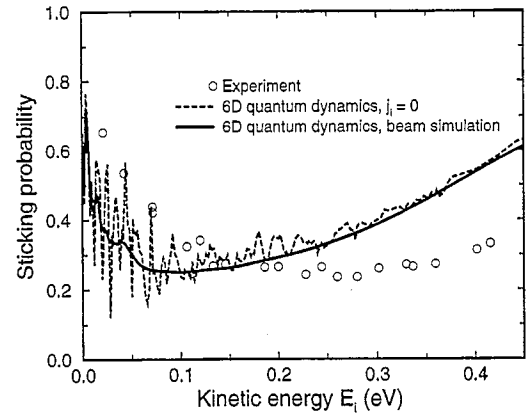


Fig. 1. Sticking probability versus kinetic energy for a $H_2$ beam under normal incidence on a Pd(100) surface. Experiment: (○) (from Ref. [24]); theory: $H_2$ molecules initially in the rotational ground state (- - -) and with an initial rotational and energy distribution adequate for molecular beam experiments (———) (from Ref. [23]).

The initial decrease results from a dynamical steering effect, which was proposed earlier (see, e.g. Refs. [25,28]), but not confirmed theoretically. Molecules approaching the surface from the gas

phase will be attracted to non-activated paths towards dissociative adsorption by the potential gradient. The slower the molecules are, the more likely it is that they actually follow these attractive paths. By increasing the kinetic energy the time that the gradient acts upon the molecules is shortened. More molecules will then hit the repulsive part of the potential without being steered to non-activated paths and will be scattered back into the gas phase [23]. This causes the decrease in the sticking probability. By further increasing the kinetic energy the molecules will eventually have enough energy to directly cross the barrier, which leads to the increase of the sticking probability at higher energies (see Fig. 1). In the quantum dynamical coupled-channel description the steering effect is reflected by the fact that at low energies more channels are needed in order to get converged results than at high energies. This indicates that there is a strong rearrangement between the different channels at low energies due to the steering.

The PES is very anisotropic with regard to the polar and azimuthal orientation of the molecule so that steering effects are also important in these degrees of freedom. The faster the molecules rotate, the more the steering and thus the dissociative adsorption probability is suppressed, because molecules with a high angular momentum will rotate out of a favorable orientation towards dissociative adsorption during the time it takes to break the molecular bond. This can already be seen in Fig. 1, where the sticking probability of the rotationally populated beam is on the average slightly lower as compared to molecules in the rotational ground state. The effect is shown in more detail in Fig. 2, which displays the orientationally averaged sticking probability

$$\bar{S}_{j_i}(E) = \frac{1}{2_{j_i}+1} \sum_{m_i=-j_i}^{j_i} S_{j_i,m_i}(E) \qquad (1)$$

versus initial kinetic energy for $j_i = 0,\ldots,4$. Fig. 2 clearly demonstrates that rotational motion indeed hinders sticking, especially at low kinetic energies, i.e. the regime where the steering effect is most efficient. This hindering effect of rotations becomes smaller, however, at kinetic energies larger than ~ 0.2 eV, where direct activated adsorption is dominant.

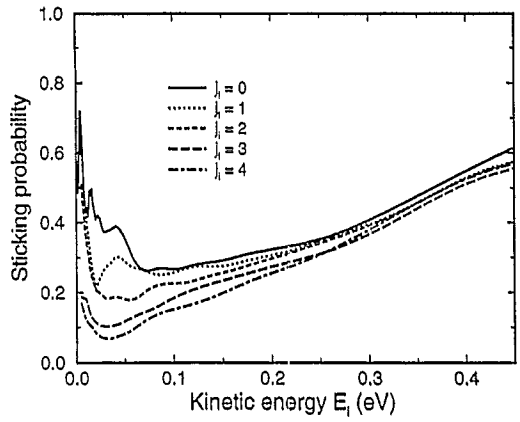


Fig. 2. Orientationally averaged sticking probability versus kinetic energy for different initial rotational quantum numbers $j_i$ of the incoming molecular beam. The molecular beams are assumed to have an energy spread of $\Delta E/E_i = 2\Delta v/v_i = 0.2$ [24] ($E_i$ and $v_i$ are the initial kinetic energy and velocity, respectively).

The suppression of the sticking probability by additional rotational motion can actually be used to discriminate between the precursor and the steering mechanism. The precursor state is usually assumed to be a physisorption state. There are only small directional forces for molecules adsorbed in a physisorption state, they can rotate almost freely [39]. The trapping probability into the physisorption state and thus the sticking probability in the precursor model should be almost independent of the initial rotational state, in contrast to the steering mechanism. Unfortunately it is not easy to prepare a molecular beam in a single quantum state. However, by seeding techniques the translational energy of a $H_2$ beam can be lowered in a nozzle experiment without changing the rotational population of the beam (the translational energy cannot be increased since there is no lighter seeding gas than $H_2$). In Fig. 3 we have plotted the orientationally averaged sticking probability versus the rotational temperature for different kinetic energies. Experimentally the rotational temperature of a $H_2$ beam can not be lower than the corresponding translational temperature (a kinetic energy of 200 meV, e.g. corresponds to a nozzle temperature of 1200 K); however, theoretically all combinations of kinetic energy and rotational temperature are feasible. For kinetic energies below ~ 40 meV there is a strong dependence of the sticking probability on the rotational temperature. By

increasing the rotational temperature the sticking probability can be decreased by more than a factor of two at these kinetic energies, which should be observable in experiment. At large kinetic energies the suppression is less pronounced, which could already be inferred from Fig. 2.

Interestingly enough, rotational motion seems to suppress sticking in general in the system $H_2$/Pd(100). We have checked this for kinetic energies $E_i \leq 0.45$ eV and rotational quantum numbers $j_i \leq 8$. Also the observed rotational cooling in desorption of $H_2$/Pd(100) [23,40] supports these findings. This situation is different in the system $H_2$/Cu(111) where a non-monotonic dependence of the sticking probability on rotational quantum number $j_i$ has been observed [2,41]: Rotational motion is found to hinder adsorption for low rotational states ($j_i < 4$) and enhance adsorption for high rotational states ($j_i > 4$) [2]. The enhancement for high $j$ states is related to the elongation of the molecular bond at the barrier position in the late barrier system $H_2$/Cu(111), which leads to a decrease of the rotational constant and thus to an effectively lowered barrier for high $j$ states [12–16,42]. In the system $H_2$/Pd(100) these late barriers, however, are absent [21].

There is still an effect that can over-compensate for the suppression of the sticking probability by rotational motion, namely the orientational or steric effect [23]. The most favorable orientation to adsorption is with the molecular axis parallel to the surface.

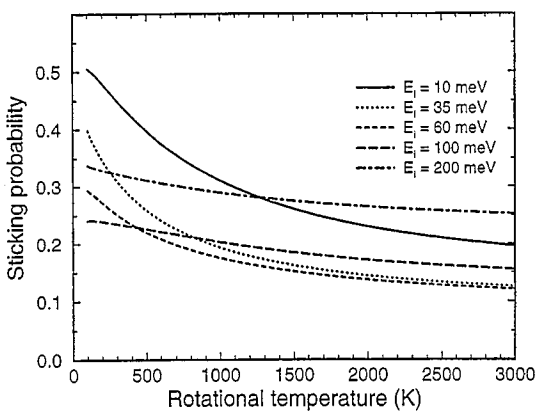


Fig. 3. Orientationally averaged sticking probability versus rotational temperature of the incoming beam for different kinetic energies.

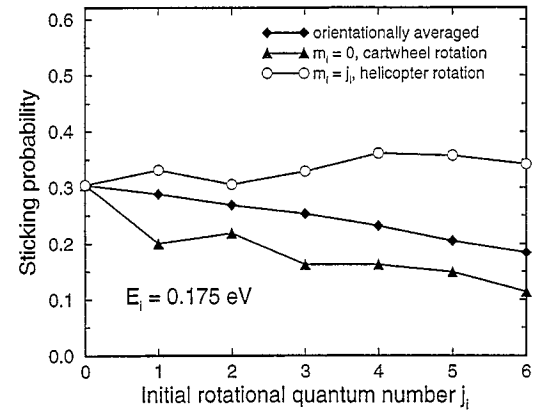


Fig. 4. Sticking probability versus initial rotational quantum state $j_i$. (◆) orientationally averaged sticking probability (Eq. (1)); (▲) $m_i = 0$ (cartwheel rotation); (○) $m_i = j_i$ (helicopter rotation). The initial kinetic energy is $E_i = 0.175$ eV.

Molecules with azimuthal quantum number $m = j$ have their axis preferentially oriented parallel to the surface. These molecules rotating in the so-called helicopter fashion dissociate more easily than molecules rotating in the cartwheel fashion ($m = 0$) with their rotational axis preferentially parallel to the surface since the latter have a high probability hitting the surface in an upright orientation in which they cannot dissociate. This steric effect, which has also been investigated in a number of model studies for purely activated adsorption [11–16], can clearly be seen in Fig. 4 where the sticking probability for one fixed kinetic energy of $E_i = 0.175$ meV is plotted. Indeed the $m_i = j_i$ data even rise with increasing quantum number $j_i$ at this relatively high kinetic energy, while the $m_i = 0$ and the orientationally averaged results are decreasing. At lower kinetic energies (not explicitly shown here), where the steering is more pronounced, the $m_i = j_i$ data also decrease.

## 4. Conclusions

In conclusion, we have reported a six-dimensional quantum dynamical study of adsorption and desorption in the system $H_2$/Pd(100) using an ab initio potential energy surface. We have shown that the initial decrease of the sticking probability with increasing kinetic energy is due to dynamical steering.

We have focused on the steering effect in the rotational degree of freedom of the hydrogen molecule and shown how the steering effect can be further confirmed experimentally. Our study demonstrates that the combination of ab initio potential energy surfaces with high-dimensional quantum dynamical calculations can lead, due to the microscopic information, to a *quantitative* as well as new *qualitative* understanding of processes at surfaces.

## Acknowledgement

We would like to thank Professor K.D. Rendulic for suggesting the detailed investigation of rotational effects in the steering mechanism.

## Note added in proof

In the meantime our prediction of the strong decrease in the sticking probability for rotationally hot hydrogen beams at transition metal surfaces has been confirmed experimentally for the system $H_2$/Pd(111) [43].

## References

[1] K.D. Rendulic and A. Winkler, Surf. Sci. 299/300 (1994) 261.
[2] C.T. Rettner, H.A. Michelsen and D.J. Auerbach, J. Chem. Phys. 102 (1995) 4625.
[3] S. Holloway, Surf. Sci. 299/300 (1994) 656.
[4] G.R. Darling and S. Holloway, Rep. Prog. Phys. 58 (1995) 1595.
[5] B. Jackson and H. Metiu, J. Chem. Phys. 86 (1987) 1026.
[6] D. Halstead and S. Holloway, J. Chem. Phys. 93 (1990) 2859.
[7] G.R. Darling and S. Holloway, J. Chem. Phys. 97 (1992) 734.
[8] S. Küchenhoff, W. Brenig and Y. Chiba, Surf. Sci. 245 (1991) 389.
[9] L. Schröter, S. Küchenhoff, R. David, W. Brenig and H. Zacharias, Surf. Sci. 261 (1992) 243.
[10] G.R. Darling and S. Holloway, Surf. Sci. 268 (1992) L305.
[11] R.C. Mowrey, J. Chem. Phys. 99 (1993) 7049.
[12] G.R. Darling and S. Holloway, J. Chem. Phys. 101 (1994) 3268.
[13] T. Brunner and W. Brenig, Surf. Sci. 317 (1994) 303.
[14] S. Kumar and B. Jackson, J. Chem. Phys. 100 (1994) 5956.
[15] J. Dai, J. Sheng and J.Z.H. Zhang, J. Chem. Phys. 101 (1994) 1555.
[16] J. Dai and J.Z.H. Zhang, J. Chem. Phys. 102 (1995) 6280.
[17] G.R. Darling and S. Holloway, Surf. Sci. 304 (1994) L461.
[18] A. Gross, J. Chem. Phys. 102 (1995) 5045.
[19] B. Hammer, M. Scheffler, K.W. Jacobsen and J.K. Nørskov, Phys. Rev. Lett. 73 (1994) 1400.
[20] J.A. White, D.M. Bird, M.C. Payne and I. Stich, Phys. Rev. Lett. 73 (1994) 1404.
[21] S. Wilke and M. Scheffler, Surf. Sci. 329 (1995) L605.
[22] S. Wilke and M. Scheffler, Phys. Rev. B 53 (1996) 4926.
[23] A. Gross, S. Wilke and M. Scheffler, Phys. Rev. Lett. 75 (1995) 2718.
[24] K.D. Rendulic, G. Anger and A. Winkler, Surf. Sci. 208 (1989) 404.
[25] P. Alnot, A. Cassuto and D.A. King, Surf. Sci. 215 (1989) 29.
[26] H.F. Berger, Ch. Resch, E. Grösslinger, G. Eilmsteiner, A. Winkler and K. D. Rendulic, Surf. Sci. 275 (1992) L627.
[27] Ch. Resch, H.F. Berger, K.D. Rendulic and E. Bertel, Surf. Sci. 316 (1994) L1105.
[28] St.J. Dixon-Warren, A.T. Pasteur and D.A. King, Surf. Rev. Lett. 1 (1994) 593.
[29] D.A. Butler, B.E. Hayden and J.D. Jones, Chem. Phys. Lett. 217 (1994) 423.
[30] D.A. Butler and B.E. Hayden, Chem. Phys. Lett. 232 (1995) 542.
[31] J.P. Perdew J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhias, Phys. Rev. B 46 (1992) 6671.
[32] P. Blaha, K. Schwarz and R. Augustyn, WIEN93, Technical University of Vienna, 1993.
[33] B. Kohler, S. Wilke, M. Scheffler, R. Kouba and C. Ambrosch-Draxl, Comput. Phys. Commun. 94 (1996) 31.
[34] W. Brenig, T. Brunner, A. Gross and R. Russ, Z. Phys. B 93 (1993) 91.
[35] Y. Chiba and W. Brenig, Surf. Sci. 306 (1994) 406.
[36] W. Brenig and R. Russ, Surf. Sci. 315 (1994) 195.
[37] A. Gross, B. Hammer, M. Scheffler and W. Brenig, Phys. Rev. Lett. 73 (1994) 3121.
[38] G.R. Darling and S. Holloway, J. Chem. Phys. 93 (1990) 9145.
[39] A. Zangwill, Physics at Surfaces (Cambridge University Press, Cambridge, 1988).
[40] L. Schröter, R. David and H. Zacharias, Surf. Sci. 258 (1991) 259; J. Vac. Sci. Technol. A 9 (1991) 1712.
[41] H.A. Michelsen, C.T. Rettner, D.J. Auerbach and R.N. Zare, J. Chem. Phys. 98 (1993) 8294.
[42] C. Engdahl and B.I. Lundqvist, Chem. Phys. Lett. 215 (1993) 103.
[43] M. Beutl, M. Riedler and K.D. Rendulic, Chem. Phys. Lett. 247 (1995) 249.