Steering and ro-vibrational effects in the dissociative adsorption and associative desorption of H$_2$/Pd(100)

Axel Gross and Matthias Scheffler

Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

The interaction of hydrogen with many transition metal surfaces is characterized by a coexistence of activated with non-activated paths to adsorption with a broad distribution of barrier heights. By performing six-dimensional quantum dynamical calculations using a potential energy surface derived from *ab initio* calculations for the system H$_2$/Pd(100) we show that these features of the potential energy surface lead to strong steering effects in the dissociative adsorption and associative desorption dynamics. In particular, we focus on the coupling of the translational, rotational and vibrational degrees of freedom of the hydrogen molecule in the reaction dynamics.

1 Introduction

It is a long-term goal in surface science to understand catalytic reactions occuring at surfaces. Obviously, the single steps of these often rather complicated processes are more effectively studied at simple systems. In particular, the dissociative adsorption and associative desorption of hydrogen on metal surfaces has served as a benchmark system, both experimentally and theoretically (see, e.g., Refs. [1, 2, 3] and references therein). Since the mass mismatch between hydrogen and a metal substrate is rather large, the crucial process in the dissociative adsorption for these particular systems is the conversion of translational and internal energy of the hydrogen molecule into translational and vibrational energy of the adsorbed hydrogen atoms. If in addition no surface rearrangement occurs upon adsorption, the substrate degrees of freedom can be neglected and the dissociation dynamics can be described in terms of potential energy surfaces (PES) which take only the molecular degrees of freedom into account.

The PES for the dissociative adsorption of a diatomic molecule neglecting the substrate degrees of freedom is still six-dimensional. These PESs now become available by elaborate density-functional calculations [4, 5, 6, 7, 8]. However, in order to understand the reaction dynamics one has to perform dynamical calculations on these potentials. Because of its light mass hydrogen has to be described quantum mechanically. Only recently it has become possible to perform dynamical calculations of the dissociative adsorption and associative desorption where *all* degrees of freedom of the hydrogen molecule are treated quantum mechanically [9]. These calculations have established the importance of high-dimensional effects in the reaction dynamics.

For example, molecular beam experiments of the dissociative adsorption of H$_2$ on various transition metal surfaces like Pd(100) [10], Pd(111) and Pd(110) [11], W(111) [12], W(100) [12, 13, 14], W(100)–c(2×2)Cu [15] and Pt(100) [16] revealed that the sticking probability in these systems initially decreases with increasing kinetic energy of the beam. High-dimensional quantum dynamical calculations have shown that steering effects can cause such an initial decrease in the sticking probability [9, 17]; it is not necessarily due to a precursor mechanism, as was widely believed. In
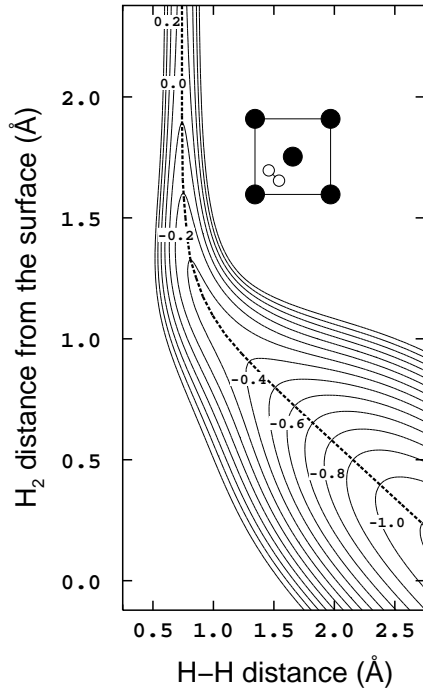
Figure 1: Contour plot of the PES along a two-dimensional cut through the six-dimensional coordinate space of $H_2/Pd\,(100)$. The inset shows the orientation of the molecular axis and the lateral H_2 center-of-mass coordinates. The coordinates in the figure are the H_2 center-of-mass distance from the surface Z and the H-H interatomic distance d. The dashed line is the optimum reaction path. Energies are in eV per H_2 molecule. The contour spacing is 0.1 eV.

this paper we briefly review the most important aspects of the steering mechanism, but mainly focus on the combined influence of the translational, rotational and vibrational degrees of freedom of the hydrogen molecule on the adsorption and desorption process. In the next section the theoretical background will be introduced before the results of the dynamical calculations will be discussed.

2 Theoretical background

The potential energy surface of $H_2/Pd(100)$ has been determined using density-functional theory together with the generalized gradient approximation (GGA) [18] and the full-potential linear augmented plane wave method [19, 20]. *Ab initio* total energies have been evaluated for more than 250 configurations [6] and have been parametrized in a suitable form for the dynamical calculations [9].

Figure 1 shows a cut through the PES of $H_2/Pd\,(100)$, where the most favourable path towards dissociative adsorption is marked by the dashed line. For this path there is no energy barrier hindering dissociation, i.e., the adsorption is non-activated. However, the majority of pathways towards dissociative adsorption has in fact energy barriers with a rather broad distribution of heights and positions, as the detailed total-energy calculations showed [6], i.e. the PES is strongly anisotropic and corrugated. This has important consequences, as will be shown below.

The quantum dynamics is determined in a coupled-channel scheme within the concept of the *local reflection matrix* (LORE) [21]. This numerically very stable method is closely related to the logarithmic derivative of the solution matrix and thus avoids exponentially increasing outgoing waves which could cause numerical instabilities. The reported calculations, which take all degrees of freedom of the hydrogen molecule into account, are still only possible if all symmetries of the scattering problem are utilized.
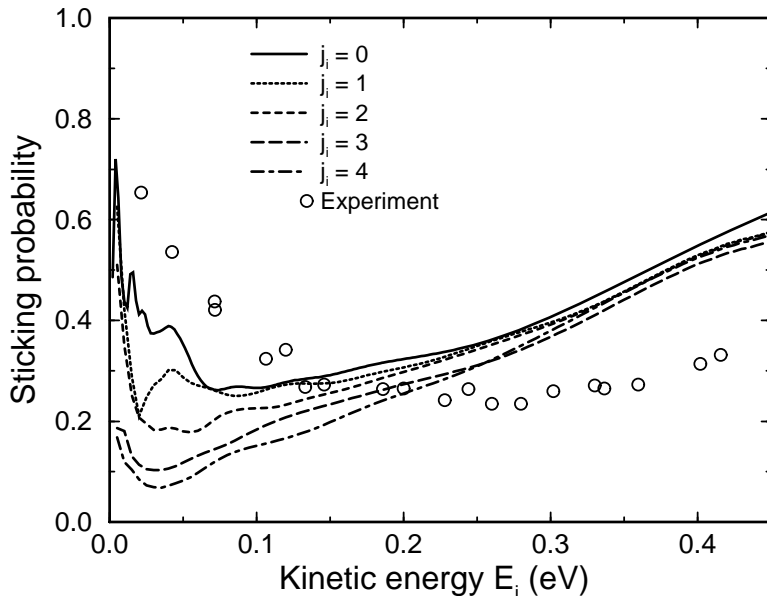
Figure 2: Sticking probability versus kinetic energy for a H_2 beam under normal incidence on a Pd(100) surface. Theory: orientationally averaged sticking probability for different initial rotational quantum numbers $0 \leq j_i \leq 4$ of the incoming molecular beam. The molecular beams are assumed to have an energy spread of $\Delta E / E_i = 2\Delta v / v_i = 0.2$ [10] (E_i and v_i are the initial kinetic energy and velocity, respectively). Experimental data (circles) are from ref. [10].

3   Results

Figure 2 presents six-dimensional quantum dynamical calculations of the sticking probability as a function of the kinetic energy of a H_2 beam under normal incidence on a Pd(100) surface for different initial rotational states averaged over the azimuthal quantum numbers. In addition, the results of a molecular beam experiment are shown [10]. Quantum mechanically determined sticking probabilities for hydrogen at surfaces with an attractive well exhibit an oscillatory structure as a function of the incident energy [9, 17, 22, 23], reflecting the opening of new scattering channels and resonances [22, 23]. These structures are known for a long time in He and H_2 scattering [24] and also in LEED [25]. For H_2/Pd(100), however, measuring these oscillations is a very demanding task. They are very sensitive to surface imperfections like adatoms or steps [26]. Since we do not focus on these oscillations here, for the results of Fig. 2 we have assumed a velocity spread of the incoming beam typical for the experiment [10] so that the oscillations are smoothed out.

The initial decrease of the sticking probability found in the experiment is well-produced for molecules initially in the rotational ground state $j_i = 0$. The high sticking probability at low kinetic energies is caused by the steering effect: Slow molecules can very efficiently be steered to non-activated pathways towards dissociative adsorption by the attractive forces of the potential. This mechanism becomes less effective at higher kinetic energies where the molecules are too fast to be focused into favourable configurations towards dissociative adsorption. This causes the initial decrease of the sticking probability. If the kinetic energy is further increased, the molecules will eventually have enough energy to directly traverse the barrier region leading to the final rise in the sticking probability.

The dynamical origin of the steering effect is reflected in the dependence of the sticking probability
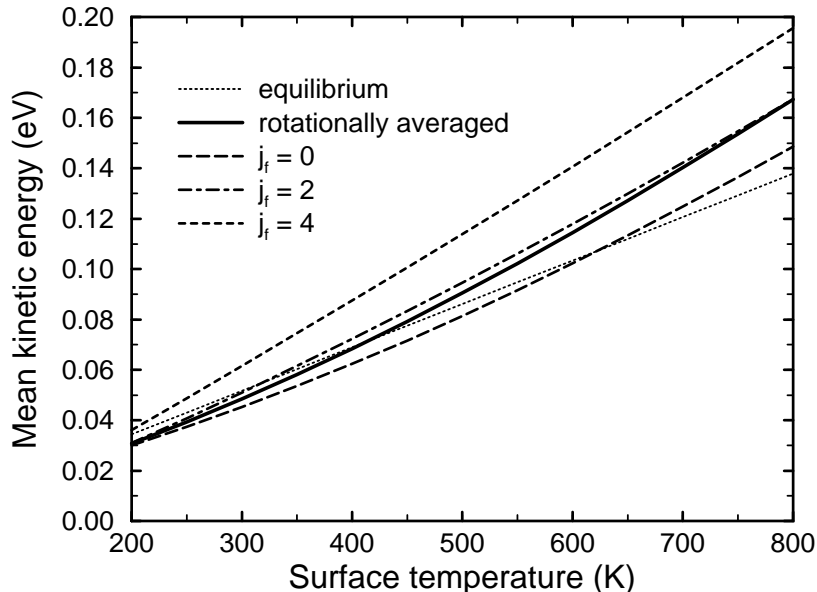
Figure 3: Mean kinetic energy of hydrogen molecules desorbing perpendicurlarly from a Pd(100) surface for different final rotational states as a function of the surface temperature. Thin dotted line: result for molecules in equilibrium with the surface temperature; thick solid line: summed over all final rotational states; dashed and dash-dotted lines: results for final rotational states $j_f = 0$, 2, 4.

on the initial rotational state of the impinging molecules. Rapidly rotating molecules will rotate out of favourable configurations towards dissociative adsorption, i.e. the steering mechanism will be suppressed. This rotational hindering is demonstrated in Fig. 2: at low kinetic energies the sticking probability decreases with increasing initial rotational quantum number j_i. At higher kinetic energies, where direct dissociative adsorption becomes dominant, rotational hindering is less important. As a consequence in this energy range the sticking probability is almost independent of the initial rotational state.

The predicted rotational hindering in the sticking probability at low kinetic energies [27] has in the meantime been confirmed by experiment [28]. The influence of the steering mechanism on the dissociation dynamics can also be demonstrated at the time-reverse process, namely the associative desorption. Invoking the principle of microscopic reversibility, any degree of freedom that hinders dissociative adsorption will in thermal associative desorption be less populated than expected for thermal equilibrium with the surface temperature T_s. At low kinetic energies increasing the initial rotational state as well as increasing the kinetic energy hinders dissociative adsorption. In desorption this leads to the so-called rotational cooling, which was found experimentally [29] and confirmed theoretically [9], as well as to translational cooling. The translational cooling is demonstrated in Fig. 3 where the mean kinetic energy in desorption as a function of the surface temperature for different final rotational states is shown. The thin dotted line corresponds to thermal equilibrium with the surface temperature. At low surface temperatures the mean kinetic energy of molecules desorbing in rotational states $j_f \leq 2$ is indeed smaller than the equilibrium value. Translational cooling is also found if the mean kinetic energy is summed over all rotational states at low surface temperatures since at these temperatures the desorption flux is mostly populated by molecules in low rotational states. For large rotational quantum numbers the steering
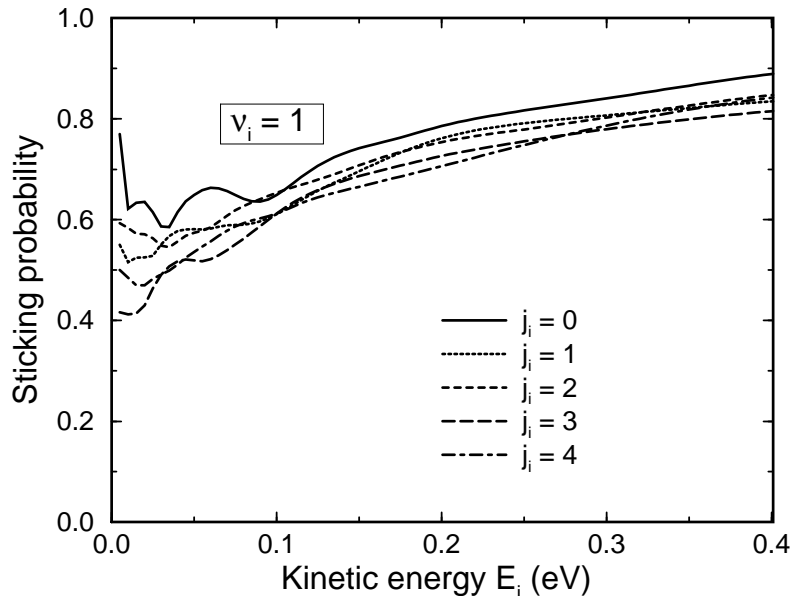
Figure 4: Sticking probability versus kinetic energy for a H_2 beam under normal incidence on a Pd(100) surface. Orientationally averaged sticking probability for different initial rotational quantum numbers $0 \leq j_i \leq 4$ for molecules initially in the first excited vibrationally state $\nu_i = 1$. The molecular beams are assumed to have an energy spread of $\Delta E / E_i = 2 \Delta v / v_i = 0.2$.

effect in adsorption is suppressed (see Fig. 2), consequently for $j_f = 4$ only translational heating is found in desorption. Equivalently, at higher kinetic energies the sticking probability rises regardless of the rotational state which leads to translational heating at higher surface temperatures for all final rotational states.

However, Fig. 3 shows that the mean kinetic energy in desorption does not differ significantly from the thermal equilibrium value. State-resolved measurements of the mean kinetic energy in desorption were done in the surface temperature range $450\,\text{K} \leq T_s \leq 850\,\text{K}$ [30]. For H_2 desorption the experiments do not show any translational heating, within the error bars the experiments are, however, consistent with our results. For D_2 desorption on the other hand, translational heating has been found [30] in good agreement with our H_2 calculations.

Interestingly, strong vibrational heating in D_2 desorption from Pd(100) has been found experimentally [31]. Usually this is associated with a so-called late barrier to adsorption as found in the system H_2/Cu [4, 5, 8]. Since the adsorption of H_2/Pd(100) is apparently non-activated [6, 10, 30], the origin of the vibrational heating has been controversely debated [32, 33, 34, 35]. Just recently we have shown that the vibrational effects in the system are caused by the lowering of the H-H vibrational frequency during the dissociation and the multi-dimensionality of the potential energy surface [36].

From Fig. 1 it is apparent that the H-H vibrational frequency is strongly lowered during the dissociation. This is also true for other pathways to dissociative adsorption. A detailed analysis of the dynamics has further shown [36] that the H-H vibrations follow the change of the vibrational frequency almost adiabatically during the dissociation. This leads to an effective vibrational–translational energy transfer, or equivalently, to an effective lowering of the PES while the molecules approach the surface. The crucial point is that this lowering depends on the vibrational state: the higher the vibrational quantum number is, the larger the effective lowering is. Thus molecules in

the first excited vibrational state experience a lower barrier range than molecules in the vibrational ground state.

In fact, for molecules in the first excited vibrational state the PES due to the lowering is so attractive that the steering mechanism is hardly operative. This is demonstrated in Fig. 4 where the sticking probability for molecules initially in the first excited vibrational state $\nu_i = 1$ for different initial rotational states j_i is shown. For $j_i = 0$ only at very low kinetic energies $E_i \lesssim 0.02$ eV there is a significant decrease in the sticking probability with increasing kinetic energy. At $E_i = 0.1$ eV the sticking probability for vibrationally excited molecules is about 2.5 times larger than for molecules in the vibrational ground state (compare Fig. 2). In desorption this leads to a population of the first excited vibrational state which is two times larger than expected for thermal equilibrium with the surface temperature at $T_s = 700$ K [36].

The fact that for vibrationally excited molecules already at small kinetic energies direct dissociative adsorption is the dominant mechanism is also reflected by the dependence of the sticking probability on the initial rotational state for vibrationally excited molecules. Fig. 4 shows that this dependence is much less pronounced than for molecules in the vibrational ground state. Due to the effectively lowered potential vibrationally excited molecules are so fast that the rotational hindering does not play any crucial role.

So far all the results presented were averaged over the azimuthal quantum number m, i.e, the results corresponded to orientationally averaged properties. Now the H_2/Pd(100) PES is strongly anisotropic with regard to the molecular orientation. The most favourable configuration towards dissociative adsorption is with the molecular axis parallel to the surface. Molecules that hit the surface in an upright position cannot dissociate, they are reflected back into the gas-phase. It is true that quantum mechanics does not allow for non-rotating, oriented molecules in the gas-phase, however, rotating molecules can show a preferential orientation. Molecules with azimuthal quantum number $m = j$ have their axis preferentially oriented parallel to the surface. It has been shown theoretically that 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 [9].

Experimentally it is hard to align a molecular beam of hydrogen. Again one can study the time-reverse process, the associative desorption. By laser-induced fluorescence (LIF) it is possible to measure the rotational alignment parameter $A_0^{(2)}(j)$ [37], which is given by

$$A_0^{(2)}(j) \;=\; \left\langle \frac{3J_z^2 - \mathbf{J}^2}{\mathbf{J}^2} \right\rangle_j \qquad (1)$$

$A_0^{(2)}(j)$ corresponds to the quadrupole moment of the orientational distribution and assumes values of $-1 \leq A_0^{(2)}(j) \leq 2$. Molecules rotating preferentially in the cartwheel fashion have an alignment parameter $A_0^{(2)}(j) < 0$, for molecules rotating preferentially in the helicopter fashion $A_0^{(2)}(j) > 0$. Figure 5 shows a comparison between experiment [38] and theory of the rotational alignment of hydrogen desorbing from a Pd(100) surface at a surface temperature of $T_s = 690$ K. Note that the experiments were done for D_2, while the calculations were performed for H_2, hence the comparison has to be done with caution. Still the agreement for $j \leq 6$ is quite satisfactory. Indeed the molecules desorb preferentially with their molecular axis parallel to the surface thus reflecting the anisotropy of the PES. Due to computational restrictions the rotational alignment could only be calculated for $j \leq 6$. For $j = 7$ and $j = 8$ the experiments show a vanishing alignment within the error bars which is rather surprising. It was argued that for these high rotational state an energy transfer from the rotations to the reaction coordinate could suppress the effect of the potential anisotropy [38]. Certainly these results deserve further clarification.
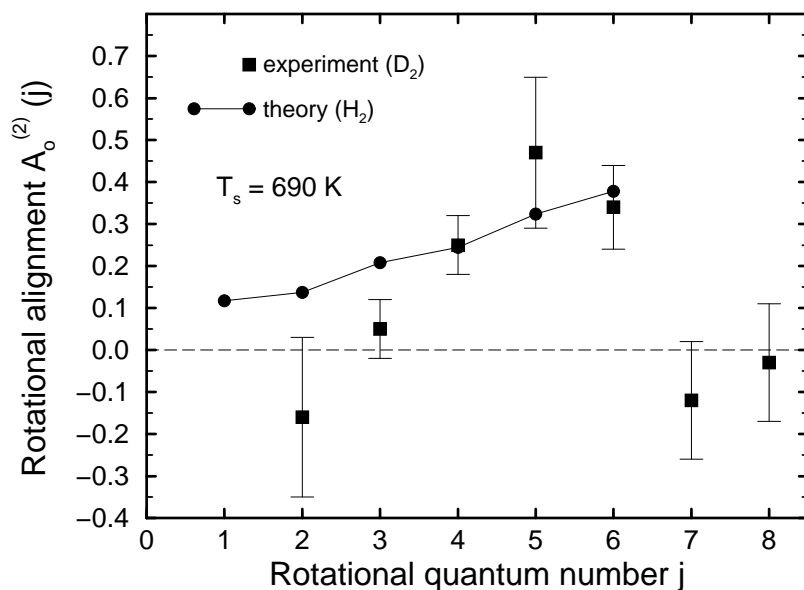
Figure 5: Rotationally alignment of hydrogen molecules desorbing from a Pd(100) surface. Boxes: experimental results for D_2 [38]. Circles: 6-D calculations for H_2.

4 Conclusions

In conclusion, we reported a six-dimensional quantum dynamical study of dissociative adsorption and associative desorption of $H_2/Pd(100)$. We have briefly reviewed the steering mechanism, in particular in the rotational coordinates, which leads to the initial decrease of the sticking probability with increasing kinetic energy. Due to the multi-dimensionality of the relevant potential energy surface the translational, rotational and vibrational degrees of freedom of the hydrogen molecule are strongly coupled during the dissociation. Our results establish the importance of a high-dimensional dynamical treatment in order to understand reactions at surfaces.

References

[1] K.D. Rendulic and A. Winkler, Surf. Sci. **299/300**, 261 (1994).

[2] S. Holloway, Surf. Sci. **299/300**, 656 (1994).

[3] G.R. Darling and S. Holloway, Rep. Prog. Phys. **58**, 1595 (1995).

[4] B. Hammer, M. Scheffler, K.W. Jacobsen, and J.K. Nørskov, Phys. Rev. Lett. **73**, 1400 (1994).

[5] J.A. White, D.M. Bird, M.C. Payne, and I. Stich, Phys. Rev. Lett. **73**, 1404 (1994).

[6] S. Wilke and M. Scheffler, Surf. Sci. **329**, L605 (1995); Phys. Rev. B **53**, 4926 (1996).

[7] S. Wilke and M. Scheffler, Phys. Rev. Lett. **76**, 3380 (1996)

[8] G. Wiesenekker, G.J. Kroes, and E.J. Baerends, J. Chem. Phys. **104**, 7344 (1996).

[9] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995).

[10] K. D. Rendulic, G. Anger, and A. Winkler, Surf. Sci. **208**, 404 (1989).

[11] Ch. Resch, H. F. Berger, K. D. Rendulic, and E. Bertel, Surf. Sci. **316**, L1105 (1994).

[12] H. F. Berger, Ch. Resch, E. Grösslinger, G. Eilmsteiner, A. Winkler, and K. D. Rendulic, Surf. Sci. **275**, L627 (1992).

[13] D. A. Butler, B. E. Hayden, and J. D. Jones, Chem. Phys. Lett. **217**, 423 (1994).

[14] P. Alnot, A. Cassuto, and D. A. King, Surf. Sci. **215**, 29 (1989).

[15] D. A. Butler and B. E. Hayden, Chem. Phys. Lett. **232**, 542 (1995).

[16] St. J. Dixon-Warren, A. T. Pasteur, and D. A. King, Surf. Rev. and Lett. **1**, 593 (1994).

[17] M. Kay, G.R. Darling, S. Holloway, J.A. White, and D.M. Bird, Chem. Phys. Lett. **245**, 311 (1995).

[18] 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**, 6671 (1992).

[19] P. Blaha, K. Schwarz, and R. Augustyn, WIEN93, Technical University of Vienna 1993.

[20] B. Kohler, S. Wilke, M. Scheffler, R. Kouba, and C. Ambrosch-Draxl, Comput. Phys. Commun. **94**, 31 (1996).

[21] W. Brenig, T. Brunner, A. Gross, and R. Russ, Z. Phys. B **93**, 91 (1993).

[22] G.R. Darling and S. Holloway, J. Chem. Phys. **93**, 9145 (1990).

[23] A. Gross, J. Chem. Phys. **102**, 5045 (1995).

[24] R. Frisch and O. Stern, Z. Phys. **84**, 430 (1933).

[25] J.B. Pendry, *Low energy electron diffraction*, Academic Press, London (1974), p. 112.

[26] A. Gross and M. Scheffler, Phys. Rev. Lett., in press.

[27] A. Gross, S. Wilke, and M. Scheffler, Surf. Sci., in press.

[28] M. Beutl, M. Riedler, and K.D. Rendulic, Chem. Phys. Lett. **247**, 249 (1995)

[29] L. Schröter, R. David, and H. Zacharias, Surf. Sci. **258**, 259 (1991); J. Vac. Sci. Technol. **A 9**, 1712 (1991).

[30] L. Schröter, Chr. Trame, R. David, and H. Zacharias, Surf. Sci. **272**, 229 (1992).

[31] L. Schröter, H. Zacharias, and R. David, Phys. Rev. Lett. **62**, 571 (1989).

[32] L. Schröter, S. Küchenhoff, R. David, W. Brenig, and H. Zacharias, Surf. Sci. **261**, 243 (1992).

[33] W. Brenig and R. Russ, Surf. Sci. **315**, 195 (1994).

[34] G.R. Darling and S. Holloway, Surf. Sci. **268**, L305 (1992).

[35] G. R. Darling, Faraday Discuss. Chem. Soc. **96**, 87 (1993).

[36] A. Gross and M. Scheffler, Chem. Phys. Lett., in press.

[37] C.H. Greene and R.N. Zare, J. Chem. Phys. **78**, 6741 (1983).

[38] D. Wetzig, R. Dopheide, M. Rutkowski, R. David, and H. Zacharias, Phys. Rev. Lett. **76**, 463 (1996).