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The fight for a reactive site

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Chapter 8

Dynamics of hydrogen dissociation on stepped platinum

Abstract

We have measured the reaction probability of H_2 and D_2 on three different stepped platinum surfaces (Pt(211), Pt(533), and Pt(755)) as a function of kinetic energy and angle of incidence using supersonic molecular beam techniques. We do not observe an isotope effect nor dependence on surface temperature. Our results for Pt(533) are in quantitative agreement with earlier results for the same system [Gee *et al.*, J. Chem. Phys. **112**, 7660 (2000)]. Characteristics of three different reaction mechanisms are observed to account for the overall reactivity. At low kinetic energy, decreasing reaction probability with increasing kinetic energy is observed, and attributed to indirect dissociation of H_2 at the step sites. At high kinetic energy, increasing reactivity with increasing kinetic energy is observed and attributed to direct, activated adsorption at terrace sites. A simple model that accounts for these reaction mechanisms implies a non-zero reactivity at the stepped surfaces at zero kinetic energy. This reactivity scales linearly with step density and is therefore ascribed to barrierless, direct reaction at step sites. Our data strongly suggest that the cross section for this mechanism is angle dependent and different from the indirect dissociative adsorption mechanism at the step. These reaction mechanisms are in agreement with earlier observations for Pt(533) [Gee *et al.*, J. Chem. Phys. **112**, 7660 (2000)] and predictions for Pt(211) [McCormack *et al.*, J. Chem. Phys. **122**, 194708 (2000)]. Applying the suggestion of Somorjai of separation of step and terrace sites [Gale *et al.*, Phys. Rev. Lett. **38**, 1027 (1977), Salmeron *et al.*, J. Chem. Phys. **67**, 5324 (1977)] we predict reactivity for Pt(533) and Pt(755) based on our Pt(211) data, and find good agreement. However, we show that this model can only be applied when the reaction mechanisms are known, and are strictly related to reactivity at steps and terraces.

8.1 Introduction

Most industrially relevant heterogeneously catalyzed reactions are performed on small particles (1-15 nm) that consist of (mostly) transition metals [1]. These particles consist of atomically flat terraces, and defects, such as step sites and kinks. The coordination of the atoms in steps and kinks is lower than the coordination of the atoms of the terraces. The importance of these special highly uncoordinated sites was emphasized already by Taylor [2].

In general, step and kink sites are believed to enhance reactivity, as was *e.g.* shown for hydrogenolysis on platinum [3], hydrogenation of ethylene on stepped nickel [4], and ammonia synthesis on ruthenium [5].

The role of steps and kinks in catalytic processes has an increasing importance when the particles are smaller, since then their density is increased with respect to the terrace sites. Electronic quantum effects inherent to nanoparticles complicate the efforts to ascribe reactivity to different areas of the catalyst, and so far only simple surface reactions are studied in detail. Examples are the hydrogenation reactions of alkenes on Pd [6] and Pt [7] particles.

In the 1970's Somorjai and co-workers pioneered an extensive study into the exchange of H_2 and D_2 on stepped platinum surfaces, investigating the role of steps in this process [8–12]. Using effusive molecular beam techniques, the authors study the difference in HD production from H_2 and D_2 on flat Pt(111) and stepped Pt(997) [8,9], Pt(332) [10–12], and Pt(553) [9, 11]. These stepped surfaces have (111) terraces separated by one atom high (110) steps, going from 4 (Pt(553)) to 8 atom-wide (Pt(997)) (111) terraces. No formation of HD is observed for Pt(111), within the detection limit (10^{-5}). On the stepped surfaces, however, HD formation is readily observed. The authors report an integrated reaction probability (HD signal integrated over total cosine distribution divided by incident D_2 signal) of 1.6×10^{-2} for Pt(997), and of 9.9×10^{-2} for Pt(553) [9]. The more steps are present, the higher the observed formation of HD. From this, the authors conclude that atomic steps at the platinum surface enhance H-D exchange by several orders of magnitude. This is in strong contrast with results of Lu and Rye [13], who found that the initial reaction probability of hydrogen dissociation is enhanced by a factor of 9 between Pt(111) and stepped Pt(211). Somorjai and co-workers contribute the difference in enhancement between their work and that of Lu and Rye to the difference in experimental techniques employed (effusive molecular beam techniques versus background dosing). Note that the step sites are different in both studies ((110) versus (100)).

In addition, Somorjai and co-workers studied the angle dependence of HD formation on the stepped Pt(332) and Pt(553) surfaces [10,11]. When the projection of the incident beam direction is parallel to the step edges, no dependence on the angle of incidence is observed. When the beam is perpendicular to the step sites, however, a significant angle dependence is observed. The reaction probability changes by roughly a factor of 2 between the extreme positions. The exchange probability is highest when impinging on the open side of the step. The authors consider the production of HD as the sum of the contributions of both step and terrace sites. The terrace sites are assumed to behave like sites on the Pt(111) surface, and the relative contribution of the steps is then estimated from the obtained results. This partitioning of step and terrace sites results in a rate of dissociative adsorption of hydrogen at step sites that is twenty times higher than on a terrace site [10]. The authors used the same assumption of separation of terrace and step sites to calculate the reaction probability ratios between steps and terraces [11]. The incident beam is divided between the available area of step and terrace sites. The reaction probability per unit area at the step site is used as a fitting parameter, and the reaction probability per unit area on the terrace sites is taken from measurements on the Pt(111) surface. From this procedure, it is calculated that the step sites are seven times more reactive for HD formation than the terrace sites at normal incidence for the Pt(332) surface [11].

By integrating the angular data over all angles of incidence the authors obtain the reaction

probability of H_2 . Using this method they find a value of 0.35 for Pt(332) and 0.07 for Pt(111), so an enhancement of a factor 5. Ertl and co-workers report an enhancement of a factor 4 for the Pt(997) surface [14]. The step density ratio for the two surfaces is $9/6 = 1.5$, while the reaction probability ratio is $5/4 = 1.25$, suggesting that the reaction probability does not scale linearly with step density [11]. However, the authors explain that due to possible differences in the pumping speed and sensitivity of the mass spectrometer for HD and D_2 , the absolute value should be regarded as correct to within 25%, weakening this claim.

A more detailed understanding of the dynamics of hydrogen dissociative adsorption on stepped platinum surfaces was obtained from quasi-classical [15–17] and quantum [18] dynamics calculations for Pt(211). In this study, three different mechanisms were observed: (i) Direct, non-activated dissociation at the top edge of the step; (ii) Trapping in weak chemisorption wells (indirect channel); and (iii) Activated reaction at the terrace. For the atom on top of the step site, the authors observe a barrier that goes to zero, enabling direct ('hit-and-stick') dissociation. At the bottom of the step a molecular chemisorption well is present, that is much deeper than a physisorption well. The molecules that get trapped in the chemisorption well, have a large chance of hopping over the one atom that separates them from the step, followed by dissociative adsorption at the step sites. The negative dependence of the reaction probability on kinetic energy as observed between 0 and ~ 0.04 eV is attributed to a trapping-mediated mechanism, and not to dynamical steering, which is observed for *e.g.* H_2 dissociation on Pd(100) [19].

Using the idea of separation of step and terrace sites, McCormack *et al.* [16] predicted the reactivity of a Pt(533) surface from their computed reaction probabilities of hydrogen dissociation on Pt(211). Using a somewhat arbitrary division between step and terrace sites, they assumed that the reaction probability on the step sites is the same for both surfaces, corrected for the number of atoms in the unit cell, and that the terrace reaction probability should be multiplied by a factor of 2 to take into account the larger terrace width of Pt(533), again corrected for the number of atoms in the unit cell. Using this method they were able to predict reasonable reaction probabilities for Pt(533), compared to the experimental data of Nunney and co-workers [20].

To test the validity of the assumption of step and terrace separation, we measured for the first time the dissociative adsorption of hydrogen on a series of stepped platinum surfaces employing supersonic molecular beam techniques. Using a better defined division between step and terrace sites we show that the crude model proposed by Somorjai and co-workers is able to predict the reactivity of Pt(533) and Pt(755) from Pt(211). We discuss the limits of the model and show under which precise conditions it can be applied.

The rest of the paper is organized as follows. In Sec. 8.2 we describe the experimental apparatus and methods employed to measure the reaction probability of hydrogen on stepped platinum surfaces. Section 8.3 presents and discusses our results. Section 8.4 summarizes our main conclusions.

8.2 Experimental apparatus and methods

Experiments were performed in a vacuum system that consists of a series of five chambers individually pumped by turbomolecular pumps [21]. A supersonic expansion of pure or

seeded H_2 (99.9999%) or D_2 (99.8%) from $\sim 1 - 4$ atm exits a 43 or 60 μm nozzle into the first chamber. A well-defined supersonic molecular beam is created by a series of skimmers and orifices, and enters the main ultra-high vacuum (UHV) chamber (base pressure $< 10^{-10}$ mbar). This chamber contains the stepped Pt single crystal surfaces, cut and polished from the same boule (99.9995%) to within 0.1° of the (211), (533), and (755) faces, respectively (Surface Preparation Laboratory, Zaandam, the Netherlands).

Cleaning procedures consist of repeated cycles of Ar^+ bombardment, followed by annealing in 2×10^{-8} mbar O_2 at 900 K to remove carbon and sulfur impurities. Subsequent annealing at 1200 K removes remaining O_2 and restores surface order. We test for surface quality by low electron energy diffraction (LEED) and temperature programmed desorption (TPD) spectroscopy of CO, NO, H_2 , D_2 and O_2 . TPD features are known to be very sensitive to impurities and cleanliness of the steps [22–28]. Cleaning cycles are repeated until no evidence for impurities is found and clear LEED images appear. From the split pattern of the LEED spots [29, 30], we determine the average terrace widths to be 2.9, 4.0 and 5.9 atoms wide, which is in agreement with the expectation of 3, 4, and 6 atom-wide terraces, respectively, for Pt(211), Pt(533) and Pt(755).

The kinetic energy of the hydrogen molecules is controlled by both the temperature of the nozzle (300–1700 K) and (anti)seeding techniques of H_2 in Ar, N_2 , and He, and D_2 in Ar, N_2 and H_2 . We determine the kinetic energy of H_2 and D_2 for all expansion conditions using time-of-flight (TOF) spectrometry. We can determine the kinetic energy in two different ways, one by fitting the TOF spectra to an appropriate form of the Boltzmann distribution (for details see Ref. [31]), or by moving the differentially pumped quadrupole mass spectrometer (QMS) over a length of 175 mm and recording spectra at different distances. The velocity of the expansion is then determined by plotting the distance versus flight time and calculating the slope of the data.

The initial reaction probability is determined using the King and Wells technique [32]. In determining the reaction probability, a complication arises from the effusive hydrogen load on the main chamber. Since the crystal temperature is well below the onset of associative desorption for small hydrogen coverages, the effusive load from the expansion chamber leads to hydrogen adsorption prior to letting the molecular beam impinge onto the crystal. We have quantified H_2 adsorption prior to the actual measurement of S_0 using integrated TPD features with a full monolayer as reference. For all data presented here, the initial hydrogen coverage was < 0.04 ML.

Using the described techniques we have determined the reaction probability at a surface temperature of 300 K. We have also measured the reactivity between 100 and 300 K in steps of 50 K for Pt(211) and Pt(533), but we found no measurable differences from the data presented here. When going to higher surface temperatures, associative desorption starts competing with dissociative adsorption.

8.3 Results and discussion

8.3.1 Reaction mechanisms

Using the above described methods we have determined the reaction probability as a function of the kinetic energy of the hydrogen molecules for the three different stepped platinum

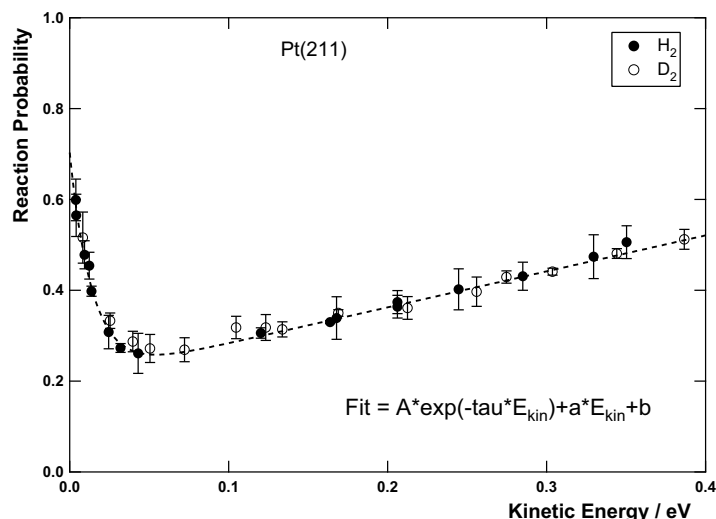


Figure 8.1: The reaction probability of H_2 and D_2 on $\text{Pt}(211)$. The data are fitted with an exponential decay and a linear dependence (dashed line). See text for details.

surfaces. In Fig. 8.1 the reaction probability of H_2 and D_2 is shown as a function of kinetic energy for $\text{Pt}(211)$ at normal incidence. In comparison to our earlier published data for the same system [33], we added more data points to the low kinetic energy regime, thus slightly modifying the shape of the curve. In all figures presenting reaction probability data in this chapter, the vertical error bars reflect two standard deviations of repeated measurements (95% confidence level). From Fig. 8.1 it can be observed that the reaction probability is isotope independent. A decrease in reaction probability with increasing kinetic energy exists between 0 and ~ 0.07 eV. Following the interpretation of McCormack *et al.* [16], we attribute this to an indirect mechanism, and not to steering. Between 0.07 and 0.4 eV the reaction probability increases with increasing kinetic energy, indicative of direct, activated adsorption.

To judge the quality of our data, we compared our measured reaction probabilities of hydrogen dissociation on $\text{Pt}(533)$ to those of Gee *et al.* [20]. This comparison is shown in Fig. 8.2. For clarity, we do not distinguish between data for H_2 and D_2 , but also for this surface we do not observe an isotope effect, in agreement with the earlier data [20]. We observe excellent agreement with respect to the absolute values and shape of the curves, especially at low kinetic energy. At high kinetic energy the results deviate slightly, possibly due to differences in the energy distribution of the supersonic molecular beam used. We do not observe any temperature dependence for any kinetic energy within our experimental error, in disagreement with the work of Gee *et al.* [20], in which a surface temperature dependence of $-4 \times 10^{-4} \text{ K}^{-1}$ was observed for a kinetic energy of 6.6 meV.

Following the three reaction mechanisms proposed by McCormack *et al.* [16], we fit our data (dashed line) with a model containing three contributions to reactivity. First, at low kinetic energy the reaction probability shows a rapidly decaying, negative dependence on energy. We fit this component with an exponential decay, as is suggested by the deconvoluted reactivity computed for this surface [16]. For direct, activated adsorption at the (111) terrace sites of the surface, a (near-)linear dependence on kinetic energy is expected, as is observed for the flat $\text{Pt}(111)$ surface [34, 35]. This linear part of the fit through the data intercepts the reactivity axis at a non-zero value, in contrast with reactivity on $\text{Pt}(111)$ which goes

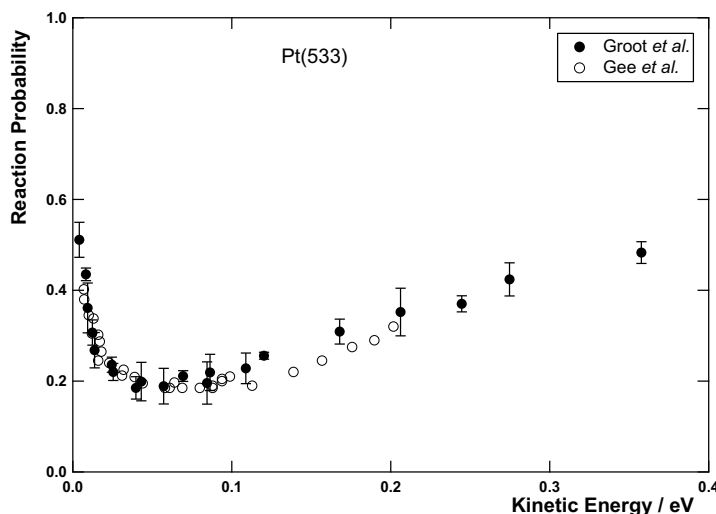


Figure 8.2: Comparison of our reaction probability of hydrogen on Pt(533) to earlier data [20].

through the origin at zero kinetic energy [34,35]. We interpret this reactivity at zero kinetic energy for stepped platinum, Pt(S), as due to adsorption of hydrogen molecules directly impinging on the step sites. This is in line with theoretical predictions that find no barrier to dissociation at these sites [16], and is the last contribution to the overall reactivity. It is assumed that over the probed energy range this contribution is energy independent. Below we show that this contribution is linearly dependent on step density. Thus, the total fit for the reaction probability is given by:

$$S_0 = A * e^{-\tau * E_{kin}} + a * E_{kin} + b. \quad (8.1)$$

Here A is the amplitude of the exponential decay, τ is its width, a is the slope of the linear contribution, and b is the intercept of the linear contribution at zero kinetic energy.

Figure 8.3 shows the reaction probability of hydrogen on Pt(533) (top left panel) and Pt(755) (top right panel), including the fit through the data which is given in Eq. 8.1. No distinction is made between results for H_2 and D_2 , as no isotope effect was observed. For Pt(755) the observed reaction mechanisms are in agreement with those observed for the other stepped surfaces. The bottom panels show the deconvoluted indirect and direct components of the reaction mechanisms for all three stepped platinum surfaces. The indirect component, corresponding to dissociation through a precursor-mediated mechanism at the step sites, is only observed at low kinetic energies, between 0 and ~ 70 meV. As expected from the corrugation of the stepped surfaces, the indirect component shows increasing reactivity following the order Pt(755), Pt(533), and Pt(211). The direct components of the reaction probability correspond to direct, activated dissociation at the terrace sites, and direct, non-activated dissociation at step sites. For comparison, Figure 8.4 shows the reactivity curves for all three stepped surfaces studied. For clarity, we do not show the separate data points, but the fit through the data only. Summarizing, at low kinetic energy (roughly between 0 and 0.1 eV) Pt(211) shows the highest reactivity, followed by Pt(533) and then Pt(755). In the regime of direct adsorption, the energy dependence for Pt(755) is the steepest, followed by Pt(533) and then Pt(211). Perhaps contrary to the general belief, Pt(755) is actually more

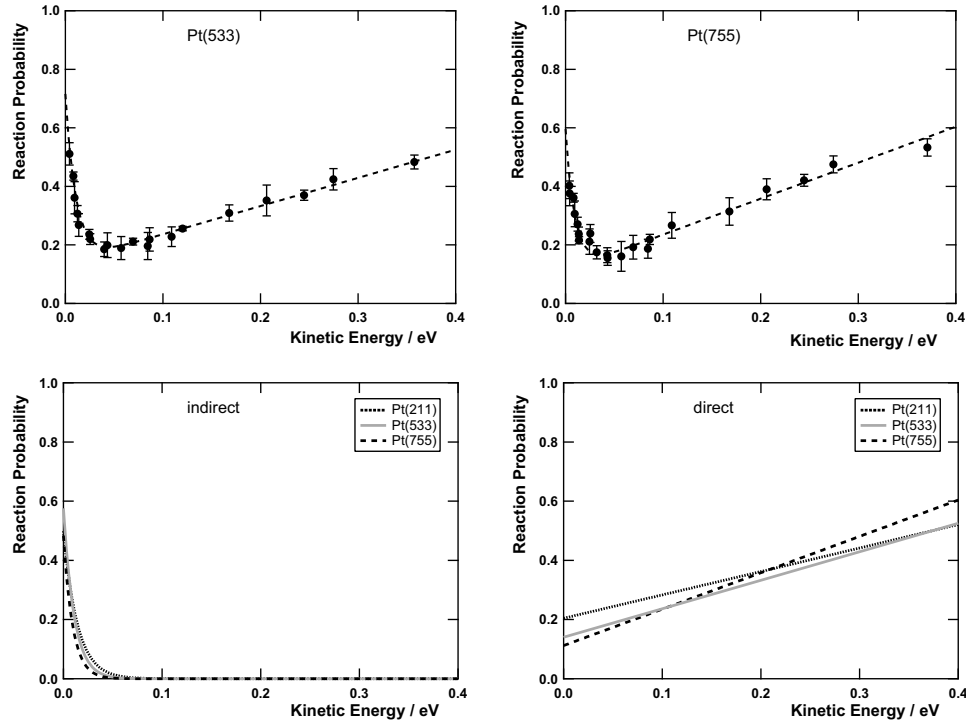


Figure 8.3: Top left panel: Reaction probability of hydrogen on Pt(533). Top right panel: Reaction probability of hydrogen on Pt(755). Bottom left panel: Indirect component of the reaction probability of hydrogen on all three stepped surfaces. Bottom right panel: Direct component of the reaction probability of hydrogen on all three stepped surfaces.

reactive than Pt(211) at high kinetic energy. To enable quantitative comparison between the different surfaces, we provide the values of the fit parameters in Table 8.1.

As described above, one component of the total reaction probability we ascribe to direct dissociative adsorption at step sites ('hit-and-stick', a non-activated pathway). If reaction probability at zero kinetic energy can indeed be assigned to direct, non-activated adsorption at step sites, one would expect this mechanism to be linearly dependent on the number of step sites present on the surface. For this reason, when plotting the reaction probability at zero kinetic energy versus the step density, we expect a straight line through the origin, since for zero step density no contribution to this mechanism is present. This analysis is shown in Fig. 8.5. From this figure it is clear that the reaction probability at zero kinetic energy versus step density is indeed linear. When extrapolating to zero step density (equivalent to

Table 8.1: Fit parameters for the fit of the reaction probability of hydrogen on stepped platinum surfaces.

Surface	A	τ	a	b
Pt(211)	0.50 ± 0.02	70 ± 3.3	0.79 ± 0.02	0.20 ± 0.004
Pt(533)	0.58 ± 0.03	91 ± 6.1	0.96 ± 0.04	0.14 ± 0.006
Pt(755)	0.48 ± 0.03	105 ± 8.1	1.2 ± 0.04	0.11 ± 0.007

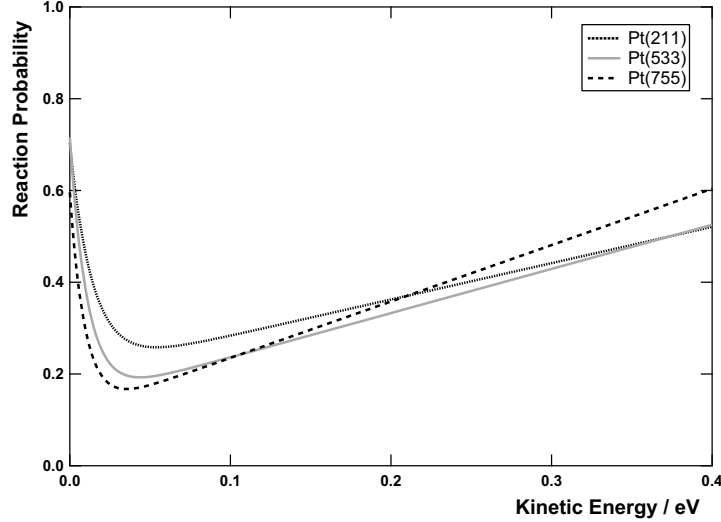


Figure 8.4: Comparison of the reaction probability of hydrogen for all three stepped surfaces investigated in this study. For clarity, only the fit through the data is shown. See text for details.

a Pt(111) surface) we predict reactivity very close to zero, in agreement with reactivity of H_2 adsorption at Pt(111) [34, 35]. The slope of the linear fit has a value of $1.34 \text{ \AA}$. Within the strict separation of reactivity due to the three mechanisms, this value, multiplied by the unit cell width of $2.8 \text{ \AA}$, represents the cross section for direct, non-activated dissociative adsorption, and corresponds to $3.7 \text{ \AA}^2$.

Figure 8.6 shows the reaction probability as a function of angle from the surface normal for low (left top panel) and high (right top panel) kinetic energy for the three different surfaces. In these experiments, the crystal is rotated relative to the molecular beam axis. For energies of $\sim 10 \text{ meV}$ and $\sim 0.35 \text{ eV}$, measurements were taken between -60° and $+60^\circ$, every 10° . The azimuthal angle of the scattering plane was normal to the direction of the step edges, and positive angles are defined as scattering into the open side of the step, as is shown in Fig. 8.6, left bottom panel, for Pt(211). At low kinetic energy ($\sim 10 \text{ meV}$), the dependence of the reaction probability on angle of incidence is approximately linear. From the angle dependent results at low kinetic energy (see Fig. 8.6, left top panel) we observe that the dependence on angle becomes steeper with decreasing step density. This indicates that for a longer terrace, it becomes more important to hit the step site at the appropriate angle. The fact that the angle dependence is observed up to angles of 60° is explained by the value of the angle between the (100) and (111) planes, which is 55° . McCormack *et al.* have suggested that a more grazing angle of incidence along the (111) plane may include trapping in the deep molecular chemisorption well that is present at the (100) step sites [16].

At high kinetic energy ($\sim 0.35 \text{ eV}$), an asymmetric dependence is observed, which is well fit by a near-linear dependence, combined with an additional $\cos^3\theta$ behavior, centered near the [111] normal. Following the analysis of Gee *et al.* we fit the data at high kinetic energy with the following formula [20]:

$$S_0(\theta) = (S_0^{111}/N)\cos^3(\theta + \theta^{111}). \quad (8.2)$$

Here, N is a factor that scales for the (111) terrace versus a Pt(111) surface. We obtain the

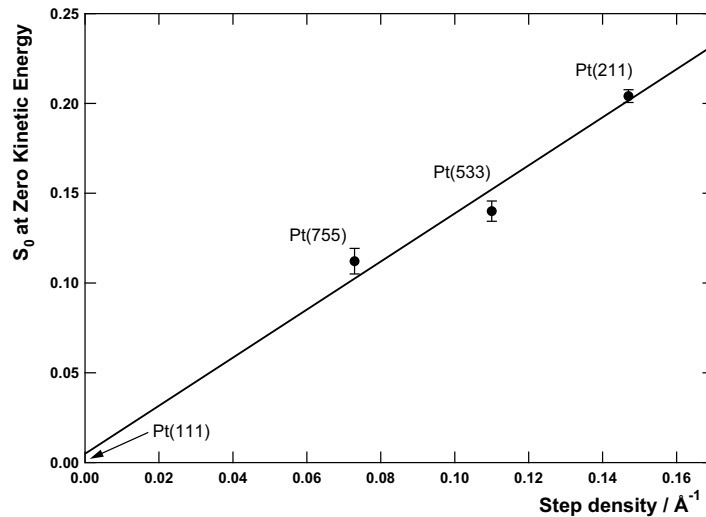


Figure 8.5: Reaction probability of hydrogen on Pt(S) at zero kinetic energy versus step density.

value of S_0 for Pt(111) at 0.39 eV and at 0.33 eV from Ref. [34]. Using values of θ of 19.5° (Pt(211)), 14.4° (Pt(533)), and of 9.45° (Pt(755)), we obtain the best fit for the parameter N . For $N = 1.2, 1.1$ and 1.1 , for Pt(211), Pt(533) and Pt(755), respectively, we obtain good agreement with the measured results at negative angles, where the (100) step is shadowed, *i.e.* for angles where the (111) terraces will dominate reaction (see Fig. 8.6). Note that Gee *et al.* found a value of $N = 0.94$ for Pt(533) [20].

Although the provided explanations for the angle dependence at low and high kinetic energies seem reasonable, we suggest an alternative view. In the low kinetic energy regime, the reactivity is dominated by two of the three reaction mechanisms: indirect dissociative adsorption and direct, non-activated dissociation. In the high kinetic energy regime reaction is dominated by direct, non-activated dissociation and direct, activated reaction. The asymmetry observed in the high kinetic energy regime beyond the normal energy dependence, suggests that a (near-)linear contribution, caused by the direct, non-activated mechanism, is present at all kinetic energies. This contribution to the reactivity can be calculated by removing the indirect component to reactivity at low kinetic energy. We then subtract the remainder, *i.e.* the direct, non-activated component, also from the high energy data. This procedure yields the reactivity attributed to direct, activated adsorption only. The results are shown in Fig. 8.6, bottom right panel. The three curves are furthermore corrected for the angle between the (111) plane and the (hkl) plane (where (hkl) is (211), (533), and (755), respectively). We find that this separation of contributions to reactivity leads to the expected behavior for the direct, activated mechanism, since we are left with a nearly symmetric curve along the (111) normal for all three surfaces. From this figure, we observe that the curves are the same for positive angles, as is expected since no interference from the step sites will occur. At the negative angles, the curves show slightly more variation. This deviation may be due to the scattering off the step when the hydrogen molecules impinge on the closed side of the steps, as shown in Fig. 8.6, left bottom panel. At these negative angles the reaction probability shows absolute values as expected from terrace lengths (for shorter terraces, a relatively larger part is shadowed by the step).

Summarizing, all available tests that we can apply to our three sets of data confirm that

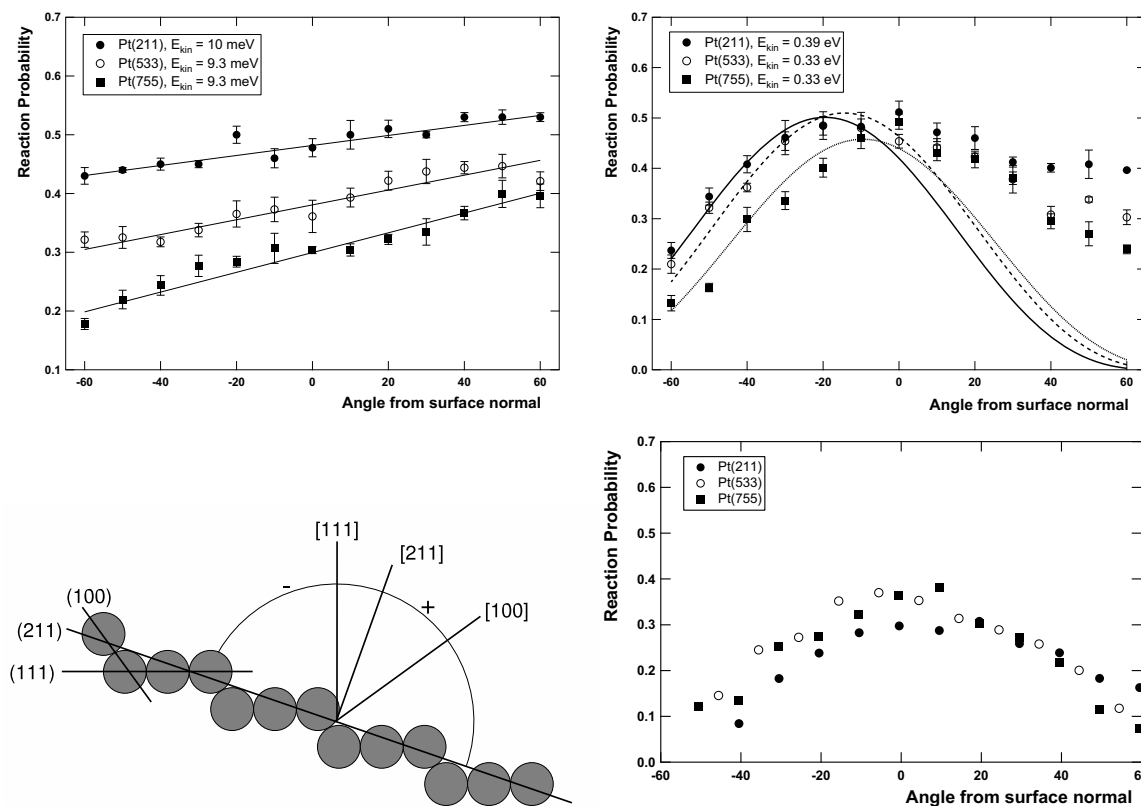


Figure 8.6: Reaction probability of hydrogen on Pt(S) at off-normal incidence for low kinetic energy (left top panel) and high kinetic energy (right top panel). In the low kinetic energy data the lines shown are merely to guide the eye. The high kinetic energy data are fitted with a $\cos^3 \theta$ dependence, as shown in Eq. 8.2. Left bottom panel: Schematic picture of the scattering angles in the angle-dependent experiments for Pt(211). Angles shown are approximate. Right bottom panel: Reaction probability of the direct, activated mechanism versus angle from surface normal, offset by the angle between the (111) and (hkl) planes. See text for details.

Table 8.2: Lengths in Å of the step and terrace for the different stepped surfaces.

Surface	Step length / Å	Terrace length / Å
Pt(211)	3.7	3.1
Pt(533)	3.4	5.7
Pt(755)	3.2	11

the separation of reactivity in three distinguishable mechanisms is valid. Furthermore, we suggest that two of these reaction mechanisms are angle-dependent, *i.e.* the direct, non-activated mechanism at step sites and the direct, activated mechanism at terrace sites.

8.3.2 Modeling reactivity on stepped platinum

We investigate the validity of the assumption of step and terrace separation suggested by Somorjai and co-workers [10, 11] and quantified by McCormack *et al.* [16]. Assuming that the step sites will have the same reactivity, and that the reactivity at the terrace will scale linearly with its length, by applying the equations suggested by McCormack *et al.* [16], we predict the reaction probability of Pt(533) and Pt(755) from the measured results of Pt(211) as follows:

$$P_{step}^{hkl} = P_{step}^{211} \frac{L^{211}}{L^{hkl}}, \quad (8.3)$$

$$P_{terrace}^{hkl} = P_{terrace}^{211} * Q * \frac{L^{211}}{L^{hkl}}, \quad (8.4)$$

$$P_{total}^{hkl} = P_{step}^{hkl} + P_{terrace}^{hkl}, \quad (8.5)$$

where hkl is either the Pt(533) or the Pt(755) surface, L is the length of the different unit cells, and Q is the parameter that describes the increase in terrace length going from Pt(211) to Pt(533) and Pt(755). In their paper, Baerends and co-workers [16] use two adversary definitions for the separation between step and terrace sites. In one case, they assumed the value of Q to be 2 for Pt(533), arguing that the amount of terrace reactivity will be twice as large for Pt(533), compared to Pt(211), because the terrace of Pt(533) has two reactive sites and Pt(211) has just one. If we extend this logic to the Pt(755) surface, Q for Pt(755) will be 4. Applying the above equations for these values of Q does not give a good description of the measured reactivity on Pt(755).

The other definition given by the authors for the length of the terrace for Pt(211) is the area along the length of the unit cell between 2.6 and 5.7 Å (see Fig. 8.7). When projecting the step and terrace lengths of Pt(211) to Pt(533) and Pt(755) taking into account the angular difference we find $Q^{533}=1.8$ and $Q^{755}=3.3$. The lengths of the step and terrace for the different surfaces are given in Table 8.2.

Using our fit to the data of Pt(211), we assign different reaction mechanisms to different sites of the surface. The linear part of the fit we attribute to direct adsorption at terrace

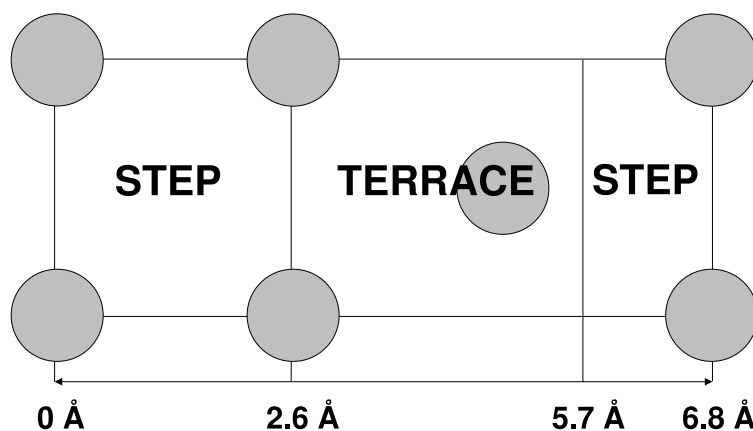


Figure 8.7: Schematic top view picture of the Pt(211) unit cell, where the division between step and terrace sites is indicated as suggested by McCormack *et al.* [16].

sites, the intercept at zero kinetic energy we attribute to direct, non-activated adsorption at step sites, and the exponential decay we assign to indirect adsorption at the steps. This results in the following formulas to predict the reaction probability of Pt(533) and Pt(755) from our measured reactivity of Pt(211):

$$P_{step}^{hkl} = (A * e^{-\tau * E_{kin}} + b) * \frac{L^{211}}{L^{hkl}}, \quad (8.6)$$

$$P_{terrace}^{hkl} = a * E_{kin} * Q * \frac{L^{211}}{L^{hkl}}. \quad (8.7)$$

The total reaction probability is then calculated using Eq. 8.5.

Figure 8.8 shows the results of the application of our model. The top panels show a comparison between the measured and predicted reaction probabilities for Pt(533), where the right panel only shows the low kinetic energy regime. The same is shown for Pt(755) in the bottom panels. When comparing the overall prediction to the measured reaction probabilities for both surfaces, we observe remarkably good agreement. When zooming in on the low kinetic energy regime, however, we observe more deviation from the measurements than at high kinetic energy. For Pt(755) the disagreement between prediction and measurement is largest. We suggest the following cause for this discrepancy. In the model the terrace is extended going from Pt(211) to Pt(533) and Pt(755) by multiplying the terrace with a certain factor. However, the terrace sites are partly responsible for dissociation at the step edges, due to the presence of the molecular chemisorption well at the bottom of the steps. The disagreement for the indirect mechanism suggests that too much reactivity actually occurring at the step sites, is attributed to the terrace sites when applying the model. In line with this observation, McCormack *et al.* have shown that the largest fraction of molecules that react through the precursor-mediated mechanism has diffused to the dissociation site at the steps from the terrace side of the terrace-step border (left border in Fig. 8.7).

For the dissociative adsorption of hydrogen on Pt(S), the model agrees remarkably well with the measurements. Although the model is based on geometric arguments and a somewhat arbitrary division between step and terrace sites, we are able to predict reactivity

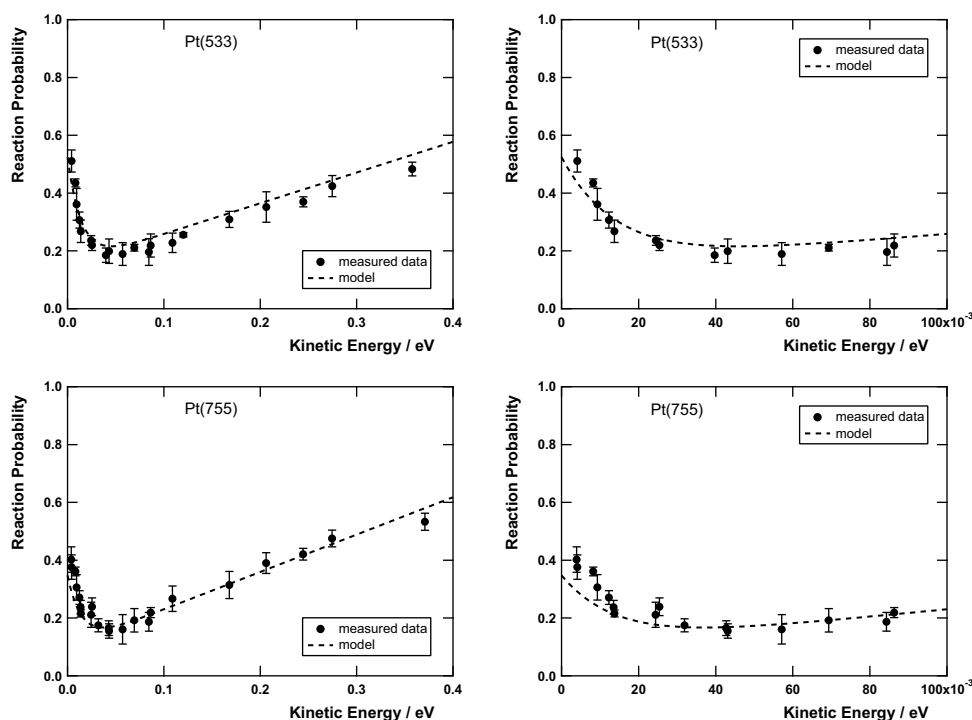


Figure 8.8: Predictions of reactivity from applying the model on Pt(533) (top panels) and Pt(755) (bottom panels) compared to measured reactivities. The right panels show a zoom-in of the low kinetic energy regime. See text for details.

accurately for larger unit cells based on the smallest. However, to be able to use this model, certain requirements needed to be fulfilled. First, detailed knowledge of the different reaction mechanisms was used from theoretical dynamics studies. Applying the reaction mechanisms observed from such theoretical studies, we fitted our data with a functional form describing these mechanisms, and we then inserted the obtained parameters in the model. Second, the reaction mechanisms that describe the overall reactivity must be strictly confined to either step or terrace sites. In situations where these requirements are not fulfilled, *e.g.* if a long-lived precursor is present that needs to diffuse over large distances before dissociating, we predict that this model breaks down. Finally, reasonable estimates must be made regarding the size of terrace and step sites.

Finally, we return to the issue of relative reactivities of step and terrace sites, as initiated by Somorjai and co-workers [11]. For overall HD formation from H₂ and D₂ on Pt(332), the authors stated that the (110) steps are 7 times more reactive than the terraces. This number was obtained from studies applying effusive molecular beam techniques. Figure 8.9 shows the fraction of the dissociative reactivity that we can strictly attribute to the step sites as a function of kinetic energy for normal incidence. It is calculated using the functional form for which the parameters were given in Table 8.1 and Eqs. 8.3 to 8.7. From this figure, it is immediately clear that the contribution of steps and terraces in the dissociation of the diatomic molecule, which is the first step in the overall exchange reaction, is strongly dependent on kinetic energy. At zero kinetic energy, this initial step in the overall reaction can only be due to the step sites on the surface. Therefore, at this kinetic energy step sites should be infinitely more reactive than terraces in any overall reaction mechanism depending

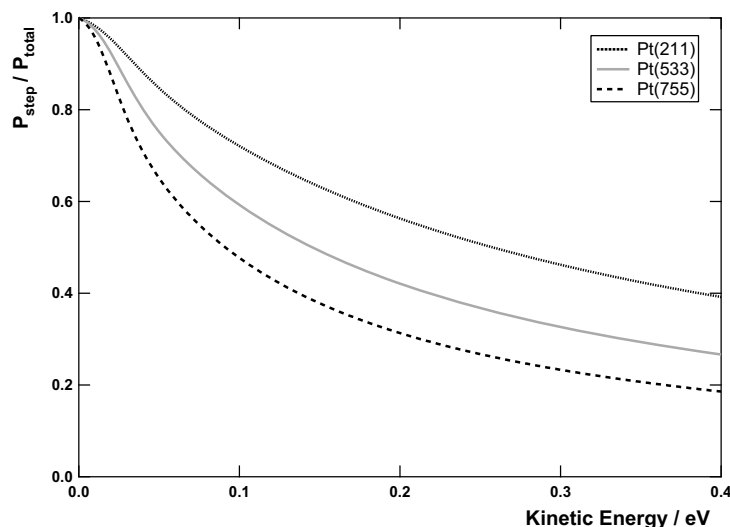


Figure 8.9: Fraction of reactivity at the step sites versus kinetic energy.

on initial dissociation. With increasing kinetic energy, dissociation occurs increasingly on terrace sites, and becomes dominant at a kinetic energy which depends on surface corrugation. When convoluting the obtained relative fractions for dissociation at step and terrace sites with a Boltzmann distribution at 300 K, thus simulating the effusive beams used by Salmeron *et al.* [11], we find that step sites are ~ 300 times more reactive than terrace sites for the dissociation only. This enhancement is much larger than was stated for the overall H/D exchange reaction. Although we note the difference in step orientations used in their and our studies, this large discrepancy suggests that other elementary steps in the HD formation process are rate-limiting.

8.4 Conclusions

Summarizing, we present the first systematic study of dynamics of H_2 dissociation on several stepped platinum surfaces using supersonic molecular beam techniques. We find an increasing reaction probability with increasing step density in the low kinetic energy regime. Three different reaction mechanisms are involved to account for the total reaction probability of hydrogen on stepped platinum: Indirect adsorption at low kinetic energy attributed to the presence of step sites, direct, non-activated adsorption at zero kinetic energy at steps, and direct, activated adsorption at terrace sites in the high kinetic energy range. These mechanisms are in agreement with theoretical predictions for Pt(211) [16] and experiments performed for Pt(533) [20]. No isotope effect nor dependence on surface temperature is observed. Quantitative agreement between our results for Pt(533) and those of Nunney and co-workers for the same surface is obtained [20]. The direct, non-activated mechanism is argued to be angle-dependent and has a reactive cross section of $\sim 3.7 \text{ \AA}^2$ for normal incidence. The direct, activated mechanism at the terraces shows a $\cos^3\theta$ dependence, indicating (near-)normal energy scaling.

Applying the assumption of separation of step and terrace sites proposed by Somorjai and co-workers in the 1970's [10, 11], we find good agreement between predictions for Pt(533)

and Pt(755) from Pt(211) and actual measurements. However, we argue that this model can only be applied if certain conditions are fulfilled. First, theoretical dynamics studies are necessary, since the reaction mechanisms that are responsible for the observed reaction probability of the surfaces should be known. In addition, these reaction mechanisms must be strictly attributed to either the step or the terrace sites, and these sites must be well-defined. In such a case, the parameters obtained from fitting the overall reaction probability can be used as inputs for the model, as is described in Sec. 8.3.

Finally, the distribution of dissociation at step and terrace sites is strongly dependent on kinetic energy. We find that steps are 300 times more reactive for dissociation than terraces for a Boltzmann distribution of 300 K. We note a large discrepancy in step reactivity for the dissociation compared to overall reactivity suggested for HD formation [11]. This raises the question whether overall reactivity differences for a multi-step reaction can truly be ascribed to differences in reactivity of steps and terraces.

References

- [1] G. Ertl, H. Knözinger, and J. Weitkamp, editors, *Handbook of Heterogeneous Catalysis*, volume 4 (Wiley-VCH Verlagsgesellschaft mbH, Weinheim, 1997).
- [2] H. S. Taylor, Proc. Roy. Soc. London A. **108**, 105 (1925).
- [3] D. W. Blakely and G. A. Somorjai, J. Catal. **42**, 181 (1976).
- [4] R. T. Vang, K. Honkala, S. Dahl, E. K. Vestergaard, J. Schnadt, E. Lægsgaard, B. S. Clausen, J. K. Nørskov, and F. Besenbacher, Nat. Mater. **4**, 160 (2005).
- [5] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).
- [6] H.-J. Freund, Catal. Today **100**, 3 (2005).
- [7] G. A. Somorjai and R. M. Rioux, Catal. Today **100**, 201 (2005).
- [8] S. L. Bernasek, W. J. Siekhaus, and G. A. Somorjai, Phys. Rev. Lett. **30**, 1202 (1973).
- [9] S. L. Bernasek and G. A. Somorjai, J. Chem. Phys. **62**, 3149 (1975).
- [10] R. J. Gale, M. Salmeron, and G. A. Somorjai, Phys. Rev. Lett. **38**, 1027 (1977).
- [11] M. Salmeron, R. J. Gale, and G. A. Somorjai, J. Chem. Phys. **67**, 5324 (1977).
- [12] M. Salmeron, R. J. Gale, and G. A. Somorjai, J. Chem. Phys. **70**, 2807 (1979).
- [13] K. E. Lu and R. R. Rye, Surf. Sci. **45**, 677 (1974).
- [14] K. Christmann and G. Ertl, Surf. Sci. **60**, 365 (1976).
- [15] R. A. Olsen, D. A. McCormack, and E. J. Baerends, Surf. Sci. **571**, L325 (2004).
- [16] D. A. McCormack, R. A. Olsen, and E. J. Baerends, J. Chem. Phys. **122**, 194708 (2005).

- [17] M. Luppi, D. A. McCormack, R. A. Olsen, and E. J. Baerends, *J. Chem. Phys.* **123**, 164702 (2005).
- [18] R. A. Olsen, D. A. McCormack, M. Luppi, and E. J. Baerends, *J. Chem. Phys.* **128**, 194715 (2008).
- [19] G. J. Kroes, A. Gross, E. J. Baerends, M. Scheffler, and D. A. McCormack, *Acc. Chem. Res.* **35**, 193 (2002).
- [20] A. T. Gee, B. E. Hayden, C. Mormiche, and T. S. Nunney, *J. Chem. Phys.* **112**, 7660 (2000).
- [21] B. Riedmüller, F. Giskes, D. G. van Loon, P. Lassing, and A. W. Kleyn, *Meas. Sci. Technol.* **13**, 141 (2002).
- [22] J. M. Gohndrone and R. I. Masel, *Surf. Sci.* **209**, 44 (1989).
- [23] J. Z. Xu and J. T. Yates, *Surf. Sci.* **327**, 193 (1995).
- [24] T. Sugisawa, J. Shiraishi, D. Machihara, K. Irokawa, H. Miki, C. Kodama, T. Kuriyama, T. Kubo, and H. Nozoye, *Appl. Surf. Sci.* **169**, 292 (2001).
- [25] R. J. Mukerji, A. S. Bolina, and W. A. Brown, *Surf. Sci.* **527**, 198 (2003).
- [26] R. J. Mukerji, A. S. Bolina, and W. A. Brown, *Surf. Sci.* **547**, 27 (2003).
- [27] R. J. Mukerji, A. S. Bolina, and W. A. Brown, *J. Chem. Phys.* **119**, 10844 (2003).
- [28] E. H. G. Backus, A. Eichler, M. L. Grecea, A. W. Kleyn, and M. Bonn, *J. Chem. Phys.* **121**, 7946 (2004).
- [29] W. P. Ellis and R. L. Schwoebel, *Surf. Sci.* **11**, 82 (1968).
- [30] M. Henzler, *Surf. Sci.* **19**, 159 (1970).
- [31] I. M. N. Groot, H. Ueta, M. J. T. C. van der Niet, A. W. Kleyn, and L. B. F. Juurlink, *J. Chem. Phys.* **127**, 244701 (2007).
- [32] D. A. King and M. G. Wells, *Proc. Roy. Soc. London A.* **339**, 245 (1974).
- [33] I. M. N. Groot, K. J. P. Schouten, A. W. Kleyn, and L. B. F. Juurlink, *J. Chem. Phys.* **129**, 224707 (2008).
- [34] A. C. Luntz, J. K. Brown, and M. D. Williams, *J. Chem. Phys.* **93**, 5240 (1990).
- [35] P. Samson, A. Nesbitt, B. E. Koel, and A. Hodgson, *J. Chem. Phys.* **109**, 3255 (1998).