Chapter 1

Introduction

1.1 Heterogeneous catalysis

Catalysis is one of the most important technologies in the modern world. Approximately 90% of all our chemicals and materials is produced using catalysis [1]. Furthermore, chemical catalysis impacts around one-quarter of the world’s gross domestic product [2]. Important examples of catalysis are the conversion of crude oil into gasoline or fuel oil, and the conversion of NO\textsubscript{x} and CO to less harmful products in our cars.

The term 'catalysis' was invented by J. J. Berzelius in 1836. He stated that: 'Many bodies have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, I shall call catalytic power. I shall also call catalysis the decomposition of bodies by this force [3].'

The term 'catalysis' was invented by J. J. Berzelius in 1836. He stated that: 'Many bodies have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, I shall call catalytic power. I shall also call catalysis the decomposition of bodies by this force [3].'

The field of catalysis can be roughly divided in two: Homogeneous catalysis, in which the catalyst and reactants are in the same phase, and heterogeneous catalysis, in which the catalyst and reactants are in different phases. The latter one is more widespread in industry, where the catalyst is usually a (metal) surface and the reactants are usually in the gas phase. The amount of surface area of the catalyst, its structure, and its composition determine the reactivity and the outcome of the reaction.

The primary objective of catalysts is to enhance the reaction rate and to yield desired products at high selectivity. Therefore, catalysts have to reduce the activation energy of the rate limiting step. As a consequence, reactions that would take a very long time to proceed without a catalyst, can now proceed on a reasonable time scale. In heterogeneous catalysis on a surface, the catalytic process is favored by the availability of active sites. These sites provide a lower energy pathway for molecules to rearrange their bonds in the breaking and reforming that is required for a chemical reaction. This is illustrated in Fig. 1.1.

In the gas phase the reaction activation energy \( E_g \) is high, largely because energy has to be expended to break bonds before the formation of new bonds begins. On the surface, however, the reacting molecules are anchored by intermediate bonds to the surface during the process, stabilizing the intermediates in the reaction. The result is that the activation barriers are generally lower than for the uncatalyzed process, and the reaction is kinetically enhanced. A catalyst thus increases reaction rates by lowering the activation barriers and speeds up the approach to equilibrium, but does not affect the equilibrium concentrations.
Figure 1.1: The energetics associated with a catalytic reaction. Activation energies: $E_a$ for adsorption, $E_s$ for surface reaction, $E_d$ for desorption, and $E_g$ for gas phase reaction. Figure adapted from Ref. [1].

In industry, catalysts usually consist of complex materials and the reactions are performed under conditions of high pressure and temperature. In the surface science studies presented in this thesis, the complexity of industrial catalysts is reduced to well-defined, single crystal surfaces. These well-defined model catalysts allow one to study the difference in reactivity of different crystal facets, or the influence of defects as steps and kinks. This difference between industrial catalysts and model catalysts used in surface science studies is known as the materials gap. In surface science studies experiments are often performed under ultra-high vacuum (UHV) conditions ($\sim 10^{-10}$ mbar). Under these conditions the surface contaminants are removed in situ and the surface remains clean for some hours afterwards. This allows one to study clean metal surfaces, and the reactivity will not be influenced by contamination of the catalyst. This difference in pressure between surface science and industrial conditions is known as the pressure gap.

1.2 Reactions of atoms and molecules on surfaces

The first step in a heterogeneous catalytic reaction is adsorption of the reacting species onto the catalyst, e.g. a metal surface. At the surface intramolecular bonds are weakened or broken. If the latter process is accompanied by formation of bonds between the fragments and the surface, it is called dissociative chemisorption. Examples of this are discussed for H$_2$ + Ru(0001) and stepped platinum, Pt(S), in this thesis. Subsequently, the adsorbed species can react with each other or with gas phase species and form new products. Generally more than one step is necessary to form the desired products, and the role of the catalyst is to lower the activation barrier of the rate determining step.

Reactions at surfaces can take place through three distinct mechanisms. The most common is the Langmuir-Hinshelwood (LH) mechanism [4,5]. In this mechanism two (or more)
1.2 Reactions of atoms and molecules on surfaces

Figure 1.2: Graphic representation of the Eley-Rideal and the Langmuir-Hinshelwood reaction mechanisms. t1 corresponds to time1, etc.

adsorbed species react at the surface, form the product and desorb. The adsorbed species are in thermal equilibrium with the surface and thus the reaction is initiated by thermal energy provided by the surface. In the second mechanism, the Eley-Rideal (ER) mechanism [6, 7], an atom from the gas phase directly collides with an atom or molecule present at the surface. Once the product is formed, it immediately desorbs, with high translational and/or internal energy. Figure 1.2 shows a graphic illustration of the LH and ER mechanisms. The third mechanism is the hot-atom (HA) or Harris-Kasemo mechanism [8]. It is an intermediate of the LH and ER mechanisms. Here, an atom coming in from the gas phase bounces around on the surface for a period of time and then reacts with an atom or molecule adsorbed on the surface before equilibrating with the surface.

On a more detailed microscopic level, the breaking and formation of bonds can be understood as the movement of a molecule on the potential energy surface (PES), which describes all molecule-surface interactions and all intramolecular interactions. Central to the computation of a PES is the Born-Oppenheimer approximation [9], where the movements of the electrons and the nuclei are separated. This is described in detail in Chapter 3, Section 3.1. Driven by its translational and internal energy a molecule might move along a certain reaction coordinate which leads to e.g. dissociation. To a first approximation, the molecule will only be able to dissociate if it possesses enough energy to overcome the reaction barrier. Due to the multi-dimensionality of the PES, the process is more complex, and also depends on the shape of the barrier, and the availability of enough energy along the reaction coordinate. For some processes reaction is enhanced by vibrational and/or rotational energy. In some systems, tunneling through the barrier occurs for light molecules, such as H₂.

To completely understand the dynamics of molecule-surface scattering, knowledge of the PES is necessary. But even if only some basic trends of the PES are known, a model of a
reaction step can be derived. Here we focus on dissociative adsorption since this is the topic of this thesis, and it is often the rate determining step in the reaction mechanism. Most dissociative adsorption processes on metal surfaces can be divided into two mechanisms, as depicted in Fig. 1.3. In the direct mechanism, a molecule impinging from the gas phase dissociates upon impact with the surface. The process is called direct, because the chemical bond is directly broken upon impact of the molecule on the surface. This process may be activated, since it involves the cleavage of a bond. The second mechanism is the trapping-mediated channel in which the molecule undergoes multiple bounces on the surface. In an inelastic collision with the surface atoms, the molecule either first dissipates sufficient energy to the surface, or it transfers its translational energy to its internal degrees of freedom, to then become trapped in a shallow physisorption or weak chemisorption well. Initiated by the thermal motion of the surface atoms, the molecule diffuses until it finds a reactive site. Since the attraction between adsorbate and surface can be weak, the molecule has a finite residence time at the surface, and it could also desorb before dissociating (trapping/desorption).

### 1.3 Dissociative adsorption of H\textsubscript{2} on a metal surface

When an H\textsubscript{2} molecule approaches a metal surface, four different processes can take place: (dissociative) adsorption, diffraction, rotational (de)excitation and vibrational (de)excitation. These four processes may be accompanied by energy transfer to phonons and/or electron-hole (e-h) pair excitations. In this thesis we study the dissociative adsorption of hydrogen on flat Ru(0001) and stepped platinum single crystals (Pt(S)). In this process, the H\textsubscript{2} molecule breaks up in two individual atoms that bind chemically to the surface.

The rate at which hydrogen dissociation takes place depends on the height of the dissociation barrier. In general, the height of the barrier to H\textsubscript{2} dissociation on top of a d-metal atom can, to a large extent, be understood as resulting from a competition between increasing overlap of the H\textsubscript{2} σ\textsubscript{u} orbital and some metal d-orbitals, decreasing overlap of the H\textsubscript{2} σ\textsubscript{g} orbital and other metal d-orbitals, and from the degree of occupation of the metal d-orbitals involved in the interactions.
The splitting of the bonding and anti-bonding states of an H$_2$ molecule interacting with the d-electrons of a metal surface.

The relevant interactions are indicated schematically in Fig. 1.4. The gas phase $\sigma_g$ H-H bonding state splits up into a broader lower-lying H$_2$ bonding/H-surface bonding state and a broader higher-lying H$_2$ bonding/H-surface anti-bonding state [10]. The gas phase $\sigma_u$ anti-bonding state splits up into a broader lower-lying H$_2$ anti-bonding/H-surface bonding state and a broader higher-lying H$_2$ anti-bonding/H-surface anti-bonding state. Due to the interaction between H$_2$ and the metal, both H-surface bonding states can be filled, i.e. the H-H bonding and H-H anti-bonding states. The filling of the H-H anti-bonding state then leads to dissociative adsorption. The position of the H$_2$ bonding/H-surface antibonding state is important in determining the reactivity of a system [10]. If this state is located below the Fermi level, the barrier to dissociative adsorption will be high (e.g. Cu), because electrons fill an orbital which is H-surface antibonding and H-H bonding, inhibiting both bonding to the surface and dissociation. If this state is located above the Fermi level, the barrier will be low (e.g. Pt and Ru). To actually dissociate on the metal surface, the H$_2$ molecule needs enough (translational) energy to overcome the barrier. In this study the reaction probability (i.e. the probability that an H$_2$ molecule that collides with the metal surface dissociates) is studied as a function of its (translational) energy.

1.4 H$_2$ + Ru(0001) and H$_2$ + Pt(S): Background and motivation

To understand the complex interactions between molecules and surfaces, one has to understand simple systems first. The interaction of H$_2$ (the smallest molecule) with a flat metal surface can serve as such a model system, and an example is studied here (see Chapter 4). In addition, more complicated systems are studied, such as flat surfaces precovered by adsorbates (Chapters 5 and 6) and stepped surfaces (Chapters 7 and 8).

The dissociation of H$_2$ on a metal surface is an elementary step in many industrial processes, and it has been studied in great detail, both experimentally and theoretically (see e.g. Refs. [11–15]). Many different metal surfaces have been investigated, but two have traditionally gained more attention, due to the extremities of their behavior. The
dissociative adsorption of hydrogen on Cu has been used as the model system for strongly activated dissociation, whereas Pd has been used as the model system for non-activated dissociative adsorption (for an overview of results see Refs. [12–15]).

In this thesis we report on the dissociative adsorption of hydrogen on Ru(0001) (Chapter 4), CO-precovered Ru(0001) (Chapters 5 and 6), and on several stepped platinum surfaces (Chapters 7 and 8).

1.4.1 \( \text{H}_2 \) dissociation on Ru(0001) and CO-precovered Ru(0001)

Ruthenium is an excellent catalyst for the production of ammonia from \( \text{H}_2 \) and \( \text{N}_2 \) [16–19]. Although the dissociation of \( \text{N}_2 \) is the rate determining step [20], the dissociation of \( \text{H}_2 \) on Ru(0001) has also found considerable attention [21–26]. For saturation coverage, adsorption takes place at the fcc threefold hollow sites [27], and the maximum coverage of H on the surface with respect to Ru atoms is 1 monolayer (1 H atom per surface Ru atom) [27–29]. The best agreement between LEED structures and calculations is obtained for a H-Ru layer distance of \( 1.10 \pm 0.06 \) Å (corresponding to an H-Ru bond length of 1.91 Å), and with \( \sim 2\% \) contraction of the Ru-Ru distance between the first and second atomic layers [27]. Disagreement of whether or not subsurface H is present on Ru(0001) [30–33] long existed. In the end it was agreed on that subsurface H is only present at surface temperatures above 320 K [34].

To study hydrogen dissociative adsorption on Ru(0001) an extensive theoretical study was done, in which density functional theory (DFT) calculations were performed and two PESs were built with different generalized gradient approximation (GGA) functionals (PW91 and RPBE) [35, 36]. The DFT study finds that the top site is the most reactive site for \( \text{H}_2 \) dissociation as predicted with both the PW91 and RPBE GGA functionals. However, PW91 predicts a higher reactivity than RPBE, with lower-energy and earlier-located reaction barriers [36]. The Ru(0001) surface is very reactive towards \( \text{H}_2 \) dissociation, as is found by a six-dimensional quantum dynamics study [35]. When comparing the reaction probabilities predicted by the two different functionals, large differences are observed. The PW91 results show a much narrower reaction probability curve and a higher reactivity. For PW91 the lowest barrier is \( \sim 0.01 \) eV, and so substantial reaction is seen for 0.02 eV (the lowest kinetic energy considered in the dynamics calculations). The highest barrier computed with the PW91 functional is 0.254 eV, and the reaction probability saturates around 0.28 eV.

For the RPBE functional, the lowest barrier is much higher than for the PW91 case, \( i.e. \) 0.085 eV, and a significantly higher kinetic energy is required for dissociative adsorption to be observed. The corrugation in the PES is also much higher, with the highest barrier being 0.437 eV. As a result, the reaction probability computed with the RPBE functional saturates around 0.5 eV.

A monotonic rise with kinetic energy is observed for both functionals, characteristic for activated systems such as \( \text{H}_2 + \text{Pt}(111) \) [37–40], \( \text{H}_2 + \text{Cu}(100) \) [41–43], and \( \text{H}_2 + \text{Cu}(111) \) [44, 45]. This behavior is expected for \( \text{H}_2 + \text{Ru}(0001) \), since a barrier height of more than zero is found.

To compare the dissociative adsorption of hydrogen on Ru(0001) with similar systems, and to shed light on the question which GGA functional better predicts the reactivity for this system, we performed an experimental study using supersonic molecular beam techniques. As a function of kinetic energy, the reactivity of \( \text{H}_2 \) and \( \text{D}_2 \) on Ru(0001) was measured for
normal and off-normal incidence. The results are shown and discussed in Chapter 4 of this thesis.

In most heterogeneously catalyzed reactions, at least two reactants interact with a solid surface simultaneously. For this reason, interactions and chemical reactions between molecules and atoms co-adsorbed on well-defined metal surfaces have received considerable attention [46–49]. The influence of adsorbates on the dynamics of adsorption and dissociation of other species from the gas phase has been studied. These studies mainly focus on the poisoning or promotional activity of pre-adsorbed atoms or molecules toward activated dissociative adsorption of different reactants [50]. Poisoning of catalysts by adsorbates is well known and for some reactions a major problem. For instance, the activity of an H$_2$-O$_2$ fuel cell is drastically reduced by the presence of CO in the feed gas. Therefore, a fundamental understanding of the influence of adsorbates on dissociative adsorption is mandatory. This thesis presents one of the first theoretical studies of this topic (see Chapters 5 and 6).

The interaction between CO and H$_2$ on Ru(0001) is a particularly interesting system because of its relevance to Fischer-Tropsch synthesis [51–53] and the methanation reaction [54–57]. In addition, CO is the main contaminant in industrial reactors.

To get more insight into chemical reactions occurring at surfaces, the co-adsorption of CO and H$_2$ is studied both experimentally [58–65] and theoretically [61,66]. The interaction between CO and H/D is repulsive, as is found from temperature programmed desorption (TPD) [63], He atom scattering (HAS) [60,63], and DFT studies [61]. No chemical reaction between CO and H/D was found [58].

The dynamics of D$_2$ dissociation on CO-precovered Ru(0001) is probed experimentally [65]. By using TPD and supersonic molecular beam techniques the reaction probability of D$_2$ is determined as a function of kinetic energy and CO-precoverage. Combined with a simple site-blocking model and information from a gas phase *ab initio* potential, insight is gained into the mechanisms by which CO modifies the D$_2$ dissociative adsorption on Ru(0001). It is found that CO blocks hydrogen dissociation and perturbs the local surface reactivity up to the nearest-neighbor Ru atoms. Non-activated reaction becomes less important with increasing CO coverage, and vanishes at $\theta = 0.33$ monolayer. In addition, at high D$_2$ kinetic energy ($> 0.36$ eV) the site-blocking capability of CO decreases rapidly. These observations are attributed to a CO-induced activation barrier for D$_2$ dissociation in the vicinity of CO molecules.

To get more insight into the site-blocking mechanisms of CO, DFT calculations are performed. By using (adaptive) nudged elastic band calculations barrier geometries for different reaction pathways are found in which all six degrees of freedom (6D) of the H$_2$ molecule are taken into account. The minimum energy path of hydrogen dissociation on CO-precovered Ru(0001) is studied in more detail by two-center projected density of states calculations and an energy decomposition analysis. These results are shown in Chapter 5.

To study the dynamics of hydrogen dissociation on this system, a PES is built and 6D dynamics (both quantum and quasi-classical) calculations are performed. A comparison between theory and experiment is done by simulating the expansion of the supersonic molecular beam taking into account the energy distribution and rovibrational population distribution of the molecular beam. These results are shown in Chapter 6.
1.4.2 Dissociative adsorption of H\textsubscript{2} on stepped platinum

The presence of defects can drastically increase the reactivity of metal surfaces toward dissociative adsorption \cite{67}, as was found for \textit{e.g.} N\textsubscript{2} on ruthenium \cite{68} and CH\textsubscript{4} on nickel \cite{69}. Density functional theory calculations have shown that the increased reactivity is caused by a lowered barrier to dissociation at the step sites \cite{69,70}.

For moderately activated systems, such as H\textsubscript{2} dissociation on platinum, experimental studies have shown that also for these systems steps enhance reactivity \cite{71-77}. Using background dosing of hydrogen, Lu and Rye measured the initial reaction probabilities for different platinum surfaces: Pt(110), Pt(100), Pt(111) and the stepped Pt(211) surface \cite{72}. They found that the initial reaction probabilities follow the order (110) > (211) > (100) > (111). The difference between flat Pt(111) and stepped Pt(211) is a factor of \(\sim 9\).

The hydrogen-deuterium exchange reaction was studied by effusive molecular beam scattering on high and low Miller index platinum faces \cite{73}. It was found that the production of HD is readily observed from the stepped surfaces. The integrated reaction probability, defined as total desorbed HD flux divided by D\textsubscript{2} flux, is \(\sim 0.1\) for these high Miller index surfaces, while HD formation was below the detection limit \((10^{-5})\) for Pt(111). When more steps are present (Pt(553) versus Pt(997), or Pt(S)-[5(111)x(110)] versus Pt(S)-[9(111)x(110)]), more HD formation is observed \((9.9 \times 10^{-2} \text{ versus } 1.6 \times 10^{-2})\) \cite{73}. From this, the authors conclude that atomic steps at the platinum surface enhance H-D exchange by several orders of magnitude. The authors attribute the difference in enhancement between their work and that of Lu and Rye to the difference in experimental techniques employed.

In addition, Somorjai and co-workers studied the angular dependence of HD formation on the stepped Pt(332) and Pt(553) surfaces \cite{74,75}. For an azimuthal angle of \(0^\circ\), \textit{i.e.} where the projection of the incident beam direction is parallel to the step edges, no dependence on the polar angle of incidence \(\theta_i\) is observed. For an azimuthal angle of \(90^\circ\), where the beam is perpendicular to the step sites, however, a significant dependence on \(\theta_i\) 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 results in a rate of dissociative adsorption of hydrogen at step sites that is twenty times higher than on a terrace site \cite{74}. The authors used the same assumption of separation of terrace and step sites to calculate the reaction probability ratios between steps and terraces \cite{75}. 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 than the terrace sites at normal incidence for HD formation on the Pt(332) surface.

By integrating the angular data over all angles of incidence the authors obtain the reaction probability of H\textsubscript{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 \cite{78}. 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.
Using supersonic molecular beam techniques, four different dissociation mechanisms were found for Pt(533) [77]: (i) Direct dissociative adsorption at terrace sites, dominant at high kinetic energy; (ii) Direct dissociative adsorption at step sites, also dominant in the high kinetic energy regime; (iii) Indirect, trapping-mediated dissociation associated with the (100) steps at low kinetic energy, dependent on surface temperature; (iv) A contribution at low kinetic energy with no dependence on surface temperature and nevertheless attributed to a trapping-mediated mechanism.

A more detailed understanding of dissociation dynamics on stepped platinum surfaces followed from the first 6-dimensional classical trajectory calculations using a DFT-based potential for H$_2$ + Pt(211) [79]. For a schematic picture of Pt(211), see Fig. 1.5. This study, and the follow-up quantum dynamical calculations [80], found support for three of the suggested mechanisms of dissociative adsorption. A single indirect mechanism with a negative dependence of reactivity on H$_2$’s kinetic energy relies on molecular chemisorption in shallow wells located near the bottom of the step with consecutive reaction at the step, a precursor-like mechanism. A decreasing reaction probability with increasing kinetic energy as found for this stepped surface at room temperature, is also observed for molecular physisorption of H$_2$ at very low surface temperatures in the same kinetic energy regime. For an overview of these results, see Ref. [81] and references therein. A second contribution was described as direct, non-activated dissociation at the step. Finally, energy-dependent, direct dissociation at terraces was identified by its well-known, increasing relation between reactivity and incident (normal) kinetic energy. For Pt(111) this relation is shown to be approximately linear, and the latter one is the only relevant mechanism [37,38].

Due to lack of available experimental data, McCormack et al. were forced to compare their theoretical predictions for Pt(211) [79,82,83] to measurements of Pt(533) [77]. Using the assumptions of Somorjai of step and terrace separation which relies on geometric arguments and a somewhat arbitrary division between step and terrace sites, they predicted reactivity of Pt(533) using their PES for the Pt(211) surface, and compared these results to the experimentally obtained ones. In Chapter 7 we directly compare experimental and theoretical results for Pt(211), removing the need for assumptions in the comparison.

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. The surfaces studied are Pt(211), Pt(533) and Pt(755). These surfaces all have one atom high (100) steps, and (111) terraces with lengths of 3, 4, and 6 atoms, respectively. 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. These results are shown and discussed in Chapter 8.

### 1.5 Outline and major results of this thesis

This thesis is divided in two parts. In the first part, the dissociative adsorption of hydrogen on a clean and CO-precovered Ru(0001) surface is studied. The experimental methods and set-up used to measure hydrogen reactivity on Ru(0001) and Pt(S) are described in Chapter 2. Chapter 3 describes the computational methods used to study the dissociative adsorption of H$_2$ and D$_2$ on the Ru(0001) surface precovered by 1/3 monolayer of CO.

The dissociation of hydrogen on a clean Ru(0001) surface is studied experimentally using supersonic molecular beam techniques. The results are presented in Chapter 4. Dissociative adsorption of H$_2$ on Ru(0001) is direct and activated, with a suggestion for non-activated adsorption. No isotope effect is observed, and normal energy scaling is obeyed. There is no measurable dependence on surface temperature within the probed range (140-180 K). We compared the dissociative adsorption on Ru(0001) to the reactivity of H$_2$ dissociation on similar metal surfaces. The dissociative adsorption of H$_2$ on Ru(0001) is similar to that on Pt(111) [37] and Ni(111) [84], although on ruthenium non-activated adsorption is strongly suggested. However, we find no clear signature of a steering- or precursor-based mechanism that favors non-activated reaction paths at low kinetic energy. For Pd, in the low kinetic energy regime, some mechanism is present leading to enhanced reactivity for decreasing kinetic energy [85]. Rhodium might be slightly affected by this mechanism [86], although not as clearly as palladium. For Ru(0001) we do not observe this mechanism down to 73 meV. If a universal mechanism exists that operates at low kinetic energies enhancing reactivity, the difference in strength of this mechanism for Rh, Pd and Ru, which have very similar masses, indicates that the mass and motion of the metal atoms are not a significant part of the mechanism.

In addition, we have compared our results to predictions of reactivity for H$_2$ on Ru(0001) from 6-dimensional quantum dynamics calculations using two different GGA functionals. It leads us to conclude that the PW91 functional yields a more accurate value for the minimum energy reaction barrier height, but this functional does not impose enough energetic corrugation on the potential. The RPBE functional appears to behave slightly better at higher collision energies, but we find significant quantitative disagreement. By doing a crude convolution of theoretical results with the energy distribution of our molecular beam, we suggest that the difference is not due to different energy resolutions between experiment and theory. However, it may be due to the use of inherently inaccurate DFT GGA functionals in the calculations, or to a dependence of the reactivity on excited rotational states, or to the neglect of phonons and e-h pair excitations in the theoretical description.

Chapters 5 and 6 describe the theoretical study of hydrogen dissociation on a CO-precovered Ru(0001) surface. In Chapter 5 different reaction pathways to dissociation are
1.5 Outline and major results of this thesis

described. To understand the mechanism of $\text{H}_2$ dissociation on this surface, two-center projected density of states calculations are done for the total system and 3 subsystems: $\text{H}_2 + \text{Ru}$, $\text{H}_2$ with only the CO overlayer and $\text{H}_2$ only. All reaction paths show a complex energy landscape. The minimum barrier for $\text{H}_2$ dissociation is found to be 0.29 eV. At this barrier the H-H bond is hardly stretched. In all reaction paths we studied, the system then moves to a molecular chemisorption minimum. To fully dissociate, the molecule has to overcome a second barrier, which may either be lower or higher than the first barrier of 0.29 eV. The existence of the second barrier is caused by the fact that due to the presence of CO, $\text{H}_2$ cannot dissociate to the threefold hollow sites, as it does on bare Ru(0001) \cite{27}. As a result, the dissociation is endoergic, as opposed to bare Ru(0001) where $\text{H}_2$ dissociation is exoergic \cite{36}.

The presence of CO on the surface increases the barrier height to dissociation compared to bare Ru(0001). Based on the energy decomposition and molecular orbital analysis we attribute the increase of the barrier mainly to an occupied-occupied interaction between the bonding $\text{H}_2 \sigma_g$ orbital and the (surface-hybridized) CO $1\pi$ orbitals. There is a small repulsive contribution to the barrier from the interaction between the $\text{H}_2$ molecule and the Ru part of the CO covered Ru surface, but it is smaller than one might expect based on the calculations of $\text{H}_2$ interacting with a clean Ru surface. Counter to intuition, the analysis suggests that the Ru surface as a subsystem is (slightly) more reactive for the reaction path studied with CO pre-adsorbed than without it. Thus, the results indicate that the influence of CO on $\text{H}_2$ dissociation on Ru is more than a simple site-blocking effect, the electronic structure of the underlying Ru (in particular the d-orbitals on the free Ru atoms) is changed.

Chapter 6 describes the building of the PES and presents the dynamics results. For the rovibrational ground state, both quantum and quasi-classical dynamics calculations were performed. They are in good agreement, which justifies the use of the quasi-classical trajectory method to perform the calculations of energy convolved and Boltzmann averaged reaction probabilities for comparison with reaction probabilities obtained in molecular beam experiments. Both quasi-classical and quantum dynamics results show a reaction probability that increases with kinetic energy. This behavior is characteristic of direct and activated adsorption and was also found experimentally for CO-precovered Ru(0001) \cite{65}. Up to $\sim 0.3$ eV no reaction is observed, which compares well to the lowest barrier we found for this system (0.29 eV).

We calculated the reactivity of several excited rotational states, and compared the results to the reaction probability of the ground state. It is found that rotational pre-excitation of $\text{H}_2$ slightly enhances the reactivity. Reactivity of the vibrational ground state is compared to that of the first excited vibrational state. Significant vibrational enhancement is observed. This is most likely due to a decrease of the $\text{H}_2$ force constant at the barrier, since the barrier is early.

Quasi-classical trajectory calculations are used to simulate the conditions of the molecular beam experiment, taking into account the rovibrational states populated and the energy distribution in the beam. The results are compared to experiment. We find that the energy distribution of the molecular beam and the populated rovibrational states increase the reactivity compared to the mono-energetic rovibrational ground state. The effect of the energy distribution is found to be larger than the effect of the rovibrational states population. However, even when taking into account these two effects, a significant discrepancy persists between theory and experiment. Both show direct adsorption, but the experimental reaction probability is significantly higher. We argue that these discrepancies could be caused by the
GGA functional used in the DFT calculations, by the presence of phonons (both for CO and Ru) and/or the presence of e-h pair excitations.

In the second part, the results of hydrogen dissociation on different stepped Pt surfaces are described. Chapter 7 shows the experimental results of the dissociative adsorption of hydrogen on Pt(211). The results are compared to theoretical predictions. Three dissociation mechanisms are observed. On the (111) plane reaction is activated and shows (near) normal energy scaling, in agreement with reaction on the flat Pt(111) surface [37,38]. The steps provide an indirect mechanism that requires accommodation of the impinging hydrogen molecules, characterized by a decreasing reaction probability with increasing kinetic energy. In addition, direct, non-activated adsorption at the steps is observed, indicated by the intercept of the reaction probability at zero kinetic energy. These observed mechanisms are in agreement with those found in computational studies for the same surface [79] and for hydrogen dissociation on Pt(533) [77]. The results are in qualitative agreement with those for Pt(533) [77], but a higher reactivity is observed for Pt(211). This is in agreement with the generally accepted idea that step sites at platinum surfaces enhance reactivity [72–75].

When comparing theory and experiment, an almost quantitative agreement is observed. However, also some discrepancies are present. First, the dominance of the indirect mechanism is significantly underestimated by theoretical studies [79,80]. This is attributed [80] to deficiencies in the PES, but it could also be due to the neglect of phonons in the theoretical study. The wells in the potential energy surface are too shallow and must trap rotationally excited molecules. At high kinetic energy the theoretical predictions significantly overestimate reactivity. Energy transfer mechanisms leading to lower reactivity as observed in the experiments could account for this disagreement. Possibilities are the excitation of phonons and/or e-h pair excitations. If they act as energy-loss mechanisms for the hydrogen molecule, the available energy to overcome barriers is reduced, resulting in lower reaction probabilities in the regime where direct adsorption is dominant.

Chapter 8 shows the results of hydrogen dissociative adsorption on Pt(211), Pt(533) and Pt(755). At low energy, the reaction probability decreases with increasing kinetic energy, characteristic of an indirect mechanism. The total reactivity decreases with decreasing step density, in agreement with the generally accepted idea that step sites at platinum surfaces enhance reactivity [72–75]. 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, activated adsorption at terrace sites in the high kinetic energy range, and direct non-activated adsorption at step sites. This latter mechanism is linearly dependent on step density. The reaction mechanisms observed are in agreement with theoretical predictions for Pt(211) [79] and experiments performed for Pt(533) [77]. No isotope effect nor dependence on surface temperature is observed. The direct, non-activated mechanism is argued to be angle-dependent and has a reactive cross section of $\sim3.7 \text{ Å}^2$ for normal incidence. The direct, activated mechanism at the terraces shows a $\cos^3\theta$ dependence, indicating (near-)normal energy scaling. The total reaction probability can be fitted using an exponential decay for the low energy regime, and a linear contribution for the high energy regime.

When comparing our data for Pt(533) to those measured before [77], we find excellent quantitative agreement, especially at low kinetic energy. In the high energy regime the results deviate slightly. This is probably caused by a different energy distribution of the supersonic molecular beams used.
Applying the assumption of separation of step and terrace sites, as proposed by Somorjai and co-workers [74,75], we predict reactivity of Pt(533) and Pt(755) using our measurements of Pt(211). When comparing the prediction based on this model to our actual measured data for Pt(533) and Pt(755) we find good agreement. 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 [75]. 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.

1.6 Outlook

1.6.1 Hydrogen dissociation on bare Ru(0001)

As reported in Chapter 4, a comparison was made between theory and experiment for H₂ dissociation on bare Ru(0001). The main results are reported in the previous section. However, when comparing experimental results to theoretical predictions, it is important to keep in mind what exactly is being compared. In a supersonic molecular beam expansion of hydrogen, rotational cooling is poor, resulting in the population of several excited rotational states [87–89]. In addition, a modest fraction of vibrationally excited molecules will be present at high nozzle temperatures. Tables 2.1 and 2.2 in the appendix of Chapter 2 give an overview of the rotational and vibrational states populated in our beam, obtained from calculating the Boltzmann fractions (see Chapter 3, Section 3.6). Heating the nozzle to higher temperatures will result in more and more broadening of the energy distribution. Hence, comparing experimental reaction probabilities that are averaged over rovibrational states and convolved with an energy distribution to theoretical predictions for mono-energetic rovibrational ground state data introduces errors. To investigate how the energy distribution of the supersonic molecular beam influences the reaction probability, we used a crude convolution of the theoretical results with our measured energy distributions. No significant difference was observed. But since the convolution was very crude, it cannot be excluded yet that the energy distribution contributes to the disagreement between theory and experiment. To be able to compare the same thing, a full molecular beam simulation should be done, including the effects of the collision energy distribution and of the rovibrational state populations.

However, at the moment we can only approximate the molecular beam simulation, since the exact rovibrational population in our beam is not known. Using the theoretical approach described in Section 3.6, the approximate rovibrational states population can be calculated. In this approach we assumed that all \( m_J \) states are equally present in the experimental molecular beam, since with the present set-up we are not able to determine the alignment
of the molecules. For a better comparison between experiment and theory, however, it is necessary to be able to exactly characterize our molecular beam in terms of rovibrational states populated. With the implementation of in situ resonance enhanced multi-photon ionization (REMPI) spectroscopy at our set-up this would be possible.

In addition, for a good comparison between theory and experiment, a clean, well-ordered single crystal surface is essential. The presence, on the one hand, of defects at the surface will significantly enhance reactivity, while, on the other hand, the presence of pre-adsorbed molecules in general will lower the measured reactivity. With our set-up as it was used in the experiments described in this thesis, we could check for surface order using low energy electron diffraction (LEED), and for cleanliness using temperature programmed desorption (TPD) spectroscopy. These techniques are in principle sensitive enough, and the fact that we can reproduce data measured at other set-ups, is a good indication for clean, well-ordered surfaces. However, to be able to better characterize our surfaces, the implementation of X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and/or scanning tunneling microscopy (STM) would be an asset.

Other possible origins of the discrepancy between theory and experiment are the neglect of e-h pairs and phonons in the theoretical study. The neglect of e-h pair excitations seems reasonable for insulator surfaces, where electronic excitations are usually prohibited by the large insulator band gap. For metal surfaces, however, low energy electronic excitations from occupied states just below the Fermi level to empty states just above the Fermi level are possible. This leads to the assumption that scattering from metal surfaces must be non-adiabatic [90]: Scattering experiments exhibit energy transfer from the nuclear motion of the adsorbate to the electrons of the metal surface. Recent experiments have indeed shown this energy transfer. The adsorption of atomic hydrogen and deuterium on a silver surface produces 'hot' electrons in the metal with hyperthermal energies [91]. Other examples of non-adiabatic effects are observed in experiments where highly vibrationally excited NO molecules are excited from an insulator, LiF, and from a metal, Au [92]. Very little vibrational relaxation is observed for NO scattering from LiF, whereas NO molecules scattering from Au loose \( \sim 1.5 \) eV of vibrational energy. A recent theoretical study [93] has shown that the inclusion of non-adiabatic effects is necessary to capture adsorbate vibrational relaxation at metal surfaces. The authors used one adiabatic potential to which e-h pair excitations were added. However, the more e-h pair excitations are present, the more deformation of the potential will occur. To take this into account, electronically excited states should be incorporated in DFT. Anyway, these studies seem to indicate that the omission of e-h pair excitations in theoretical studies is problematic. On the other hand, for H\(_2\) dissociation and scattering on Pt(111) it was found that the neglect of e-h pair excitations is justified [94].

In the theoretical study of hydrogen dissociation on Ru(0001) phonons are also neglected. After relaxing the Ru slab, the surface is kept frozen, and only the six degrees of freedom of the H\(_2\) molecule are taken into account. Although experiments did not find a surface temperature dependence in the range studied (140-180 K), phonons cannot be ruled out. Including phonons in the theoretical study can be done through the use of the surface oscillator model [95–99]. In this model, phonons are modeled by making the molecule-surface interaction potential dependent on a coordinate \( d \), associated with the oscillator, in the center-of-mass coordinate \( Z \) of the molecule, and by adding a harmonic term in \( d \), as follows:

\[
V(X,Y,Z,r,\theta,\varphi,d) = V(X,Y,Z - d,r,\theta,\varphi) + Cd^2/2.
\]

Here \( C \) is a so-called collective model parameter [95,100]. The inclusion of phonons using the surface oscillator
model transforms the problem from 6D to 7D.

The most likely culprit for the discrepancy observed between theory and experiment are the GGA functionals used. Recent studies on different types of systems tend to indicate the RPBE functional as the best candidate for accurately predicting experimental results, since the PW91 functional predicts too high chemisorption energies to a larger extent than the RPBE functional [70,101–103]. However, for the system discussed here we observe that the RPBE functional overestimates the dissociation barrier. Recent results on H$_2$ + Cu(111) and Cu(100) suggest that a GGA functional consisting of a mixture between the RPBE and PW91 functionals (so-called specific reaction parameter (SRP) DFT) is able to predict reactivity within chemical accuracy [104]. So the next step to see whether better agreement between theory and experiment could be obtained would be to employ SRP DFT for this system.

### 1.6.2 Hydrogen dissociation on CO-precovered Ru(0001)

To be able to better compare experiment and theory, a molecular beam simulation was done for the H$_2$ + CO/Ru(0001) system. The main results are discussed in Sec. 1.5. Even for the full molecular beam simulation, a significant discrepancy persists between theory and experiment. From this we can conclude that this discrepancy is not caused by the energy distribution in the molecular beam. As explained in the previous section, due to incomplete characterization of the molecular beam used in the experiments, we cannot yet rule out that part of the discrepancy between theory and experiment is caused by the population of excited rotational states in the beam. Other possible experimental issues such as surface characterization, are also addressed in the previous section.

In the calculations we used the RPBE GGA functional. Although this functional did not obtain good agreement between theory and experiment for the H$_2$ + Ru(0001) system, at the start of this project, no proof was available that other standard GGA functionals performed better. Recently, chemical accuracy was obtained for H$_2$ dissociation on Cu(111) and Cu(100), using SRP DFT, as described in the previous section. It is likely that a large part of the disagreement with experiment is due to the use of the RPBE functional, and that much more accurate results can be obtained using the SRP approach. Another possible reason for the disagreement between theory and experiment is the neglect of e-h pair excitations. For elaboration on this, we refer the reader to the previous section.

A likely origin for the discrepancy between theory and experiment is the neglect of phonons, both of the CO molecule and the Ru surface. After relaxing, the CO molecule and Ru slab are kept frozen. However, a recent study of H$_2$ dissociation on H-precovered Pd(111) and Pd(100) [105] showed that to obtain an accurate picture, movement of the pre-adsorbed H atoms and of the first layers of Pd surface atoms needs to be taken into account. For our system it is possible that the CO molecules move to make room for the impinging H$_2$ molecules. Whether this is indeed the case could be explored experimentally by STM, taking images before and after the impinging hydrogen molecules hit the surface. Full incorporation of movement of CO in the theoretical simulation will be difficult. However, in principle this can be done by performing ab initio molecular dynamics (AIMD) simulations as done by Gross and Dianat [105]. So the next step to obtain better agreement between theory and experiment would be the incorporation of the degrees of freedom of CO into the calculations.
1.6.3 Hydrogen dissociation on stepped platinum

Chapter 7 describes the comparison between theory and experiment for the dissociative adsorption of hydrogen on Pt(211). Our experimental results show the same three reaction mechanisms that were suggested by theory [79], \textit{i.e.} direct dissociation at step and terrace sites, and indirect adsorption at step sites. The almost quantitative agreement between theory and experiment is encouraging, although discrepancies still exist, as is addressed in Sec. 1.5.

Especially at high kinetic energy, the theoretical predictions overestimate the reaction probability. Therefore, the explanations for this discrepancy must be found in energy transfer mechanisms to account for the lower reactivity observed in our measurements. One possibility could be the effect of population of excited rotational states in the experiment. Experimentally, high kinetic energies are obtained from heating the nozzle, introducing the population of excited rotational states. If these excited rotational states have lower reactivity, this could account for the lower reaction probability as observed in experiments versus theory. However, quasi-classical calculations have shown that there is little difference in reactivity between $J = 0$, $J = 1$ and $J = 2$ states [83]. Therefore, other explanations must be found for the discrepancy between theory and experiment in this energy range, looking for additional energy transfer mechanisms to account for the lower reactivity observed in our measurements. Possibilities are phonon and e-h pair excitations, which are neglected in the theoretical study. Taking into account the effect of the energy distribution of the supersonic molecular beam would be expected to \textit{increase} the theoretical reaction probability, thus making the agreement worse instead of better. For a detailed discussion of these possibilities we refer to Section 1.6.1.

Chapter 8 describes the dissociative adsorption of hydrogen on several stepped platinum surfaces, with (111) terrace lengths ranging from 3 to 6 atoms. The investigated surfaces consist of one atom high (100) steps, which turn out to be very reactive. Studies of Somorjai and co-workers of stepped platinum surfaces with (110) steps [73–75] using effusive molecular beam techniques showed that the activity of the (110) steps is higher than that of the Pt(110) surface [75]. This might suggest that the presence of terraces influences the reactivity of step sites by enhancing it, indicating that a separation between terrace and step sites breaks down. Whether this is the case could possibly be investigated by temperature programmed desorption spectroscopy. Hydrogen molecules are expected to be more strongly bound at step sites, resulting in a higher desorption temperature. If step and terrace sites can indeed entirely be separated, one would expect to find the same desorption temperatures for the step and terrace sites, respectively, on all our different stepped platinum surfaces, the only difference being the amount of hydrogen adsorbed on step and terrace sites. The more steps are present, the higher the integrated peak signal for step desorption should be. At the moment we are in the process of doing these experiments in our laboratory.

In addition, performing the same supersonic molecular beam experiments for surfaces with (110) steps (\textit{e.g.} Pt(553)) as we did for the surfaces with (100) steps could give an indication whether significant differences in reactivity exist for the different step geometries.

From our studies we find that steps are 300 times more reactive for $\text{H}_2$ dissociation than terraces for a Boltzmann distribution of 300 K. For the process of HD formation, Somorjai and co-workers found an enhancement of a factor 7 between steps and terraces [75]. To shed light on this discrepancy, and to answer the question whether overall reactivity differences for
a multi-step reaction can truly be ascribed to differences in reactivity of steps and terraces, we also studied the HD formation process. Using supersonic molecular beam techniques, we studied the formation of HD from H$_2$ and D$_2$ for all three stepped surfaces. At the moment we are in the process of analyzing our data.

References


Chapter 1. Introduction


