Hydrogen dissociation on metal surfaces: A semi-empirical approach

Nour Ghassemi, E.

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CHAPTER 1

Introduction

1.1 Reactions of molecules on surfaces

Molecule surface interactions are very important, not only in many industrial applications [1], but also in our daily life. There are very simple examples of molecule-surface interactions in the world around us. For example, when an iron chain has turned to red, oxidation reactions have taken place: iron reacts with the oxygen in the air and get rusted in a humid environment. Many physicists and chemists study these kinds of phenomena to understand how gas or liquid molecules interact with solids.

The simplest aspect of a chemical reaction based on our elementary background of chemistry knowledge is that two molecules approach each other and climb the potential energy barrier, their bonds get pulled apart in the transition state and finally separate. New products are formed. However, complexity is added in chemical reactions when the reactant is a metal surface [2]. In the meantime, it is known that catalysts reduce the energy required for material productions. Catalysts create an alternative energy pathway to increase the speed and outcome of the reaction. It would be difficult to imagine our industrialized world without catalysts. For example, catalytic converters in vehicles convert pollutants in the exhaust to safer substances [3]. Catalytic production of ammonia (the so-called Haber-Bosch process [4]) enabled a dramatic increase of the agricultural production [5]. Heterogeneous catalysis, which has a crucial role in chemical technology, is a type of catalysis in which the molecules involved in the catalytic reaction are in a different phase (often in the gas phase) and the catalyst is often a solid metal surface. The understanding of catalysis has rapidly increased in the last decades [6]. However, there are many complexities. The catalyst itself may have a very complicated structure, and understanding catalysts under real working conditions often involving high temperature and pressure is not easy.

Surface science techniques have already enabled us to understand many catalytic reactions both from an experimental and theoretical perspective. One of the most well-known examples is the understanding of the reaction mechanism for ammonia synthesis, for which Gerhard Ertl has been awarded the Nobel Prize in chemistry [7]. The experimental works on this process, also known as the Haber-Bosch process, lead to the conclusion that the rate-

limiting step of this process is the dissociative chemisorption of nitrogen on the catalyst surface. For the Haber-Bosch process commonly iron or ruthenium based catalysts are used.

The modern instruments provide the facilities to clean and orient catalyst samples with very high accuracy. To avoid polluting atoms and molecules which might deposit on a surface, the samples are kept at very low pressure under ultrahigh vacuum conditions. Clean and well-defined flat surfaces reduce the complexity of the system to a great extent. Several spectroscopic, diffraction and microscopic methods are used to study catalysis. Supersonic molecular beams experiments are especially useful among the methods to study catalysts. The translational energy of the gas molecules can be controlled by changing the nozzle temperature, or by seeding with other gases. The angle of incidence is often controlled in the molecular beam experiments. These experiments allow measuring sticking probabilities of gas molecules to a surface as a function of all these observables (*i.e.*, incidence energy, angle, or in some cases initial rotational or vibrational state of the gas molecule).

A large amount of information on the gas surface interaction can thus be obtained from molecular beam experiments. It is also very beneficial to understand the underlying potential energy surface (PES) for the molecule-surface interaction. However, based on the experimental results only, understanding microscopic details of the interaction is very difficult. Theoretical modeling and molecular dynamics simulations are now able to reproduce molecular beam experiments, which is crucial to understanding the details of the molecule-surface interaction. Molecular dynamics simulations are often cheaper than the experiments. Molecular beam simulation in some cases is able to match experiments very accurately, however in other cases there is still plenty of room for improvement. From another point of view, molecular beam experiments can be of help with the development of theoretical models for the molecule-surface interactions [8]. In the absence of an accurate *ab initio* method for computing molecule-metal surface interactions, it seems that the best can be achieved by a combination of both experiments and theoretical modeling to understand and develop new catalysts [8].

Modeling a reaction on a surface is typically a two-step process. First, the interaction energy of the molecule on the surface is computed for various configurations and then used to construct a PES. In this step, the most important challenge is to obtain a reaction barrier within chemical accuracy. The next step is to calculate the dynamics, *i.e.*, to determine how

the molecule moves on the PES and exchanges energy until the products are formed. This two-step procedure amounts to modeling the reaction with the so-called Born-Oppenheimer (BO) approximation [9]. In molecule-metal surface interactions, the continuum of electronic states of a metal surface can be an extra energy exchange channel between molecule and surface. A small amount of energy can be transferred from molecular degrees of freedom (DOF) to the electrons lying just under the Fermi level. This generates an electron-hole pair. The accurate description of the effect of electron-hole pair excitation on molecule-surface reactions is an important challenge to achieving chemical accuracy for some molecule-surface reactions. Multiple electronic states and coupling between them may have to be taken into account.

When a molecule meets a surface, various events can occur. The most common events are shown in Figure 1.1. The process of adsorption of molecules or atoms is one of the key steps in molecule-surface reactions. A molecule can be adsorbed to a surface through several mechanisms: (a) dissociative chemisorption, in which a bond of an incoming molecule is broken and two new bonds are formed between the fragments and surface atoms, (b) abstraction, in which a bond of the incoming molecule is also broken but only one fragment is absorbed to the surface while the other fragment escapes to the gas phase, (c) molecular adsorption, in which a molecule gets adsorbed on the surface as a whole, either by chemisorption or physisorption, but the bond in the molecule is not broken. The combination of adsorbed fragments is also possible. Three other events are shown in the figure : (d) the Langmuir-Hinshelwood reaction, in which two fragments that are accommodated to the surface meet each other, form a new bond and the newly formed molecule desorbs (This mechanism can be regarded to be the reverse of dissociative chemisorption, and is also called associative desorption.), (e) Eley-Rideal reaction, in which a fragment coming from the gas phase collides with an adsorbed fragment, forms a new bond and the molecule that is formed in this way, desorbs, (f) hot atom reaction, in which a fragment coming from the gas phase collides with the surface and makes several bounces while it is not yet in thermal equilibrium with surface, collides with an other adsorbed fragment on the surface which is in thermal equilibrium with it, forming a new bond and the molecule formed desorbs. Dissociative chemisorption is an elementary step in many catalyzed reactions and often a rate-limiting step in the overall reaction [7]. This reaction is therefore of particular interest in the field of heterogeneous catalysis.
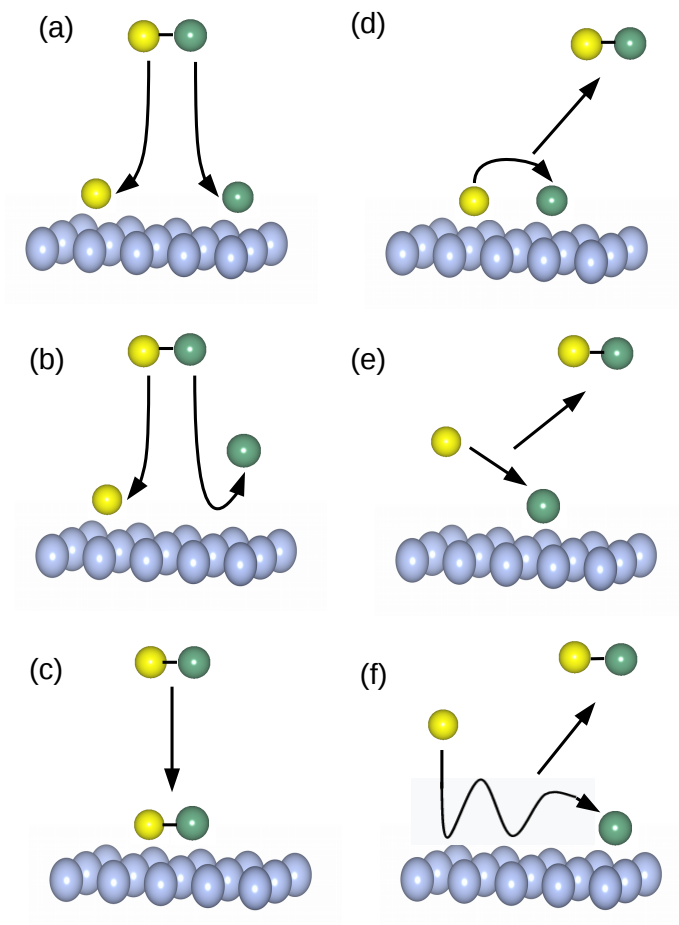
Figure 1.1: Different mechanisms for molecule-surface reactions: (a) dissociative chemisorption, (b) abstraction, (c) molecular adsorption, (d) Langmuir-Hinshelwood, (e) Eley-Rideal and (f) the hot-atom mechanism.

1.2 Scattering of molecules from surfaces

To study the chemical reaction occurring at a surface, it is conceptually important to understand the scattering and adsorption of a molecule on the surface. A relatively simple molecule like hydrogen scattering from or getting adsorbed on a surface can serve as an ideal model system to study. There are several reasons for this. First, a hydrogen molecule is a homonuclear diatomic molecule and the simplest molecule for which dissociative chemisorption occurs. Second, in spite of the fact that phonon and nonadiabatic effects play a role in dissociative and reactive scattering, both thermal surface atom displacements due to phonons and electron-hole pair excitations are expected to have a small effect on the dissociative chemisorption of hydrogen on metal surfaces [10]. The full discussion of these effects and a detailed overview of theoretical results on H_2 dissociation on and scattering from a surface can be found in Refs. [10–13]. For a H_2-metal surface system we can then assume reaction to take place on a ground state PES, and on a static surface. Briefly, it has been argued that electron-hole pair excitation can be neglected for H_2-metal systems because, for H_2 dissociation on Pt(111) and using a single PES it was possible to accurately describe both reaction and diffractive scattering [14]. Furthermore, electron-hole pair excitation effects were studied explicitly in H_2 dissociation on Cu(111) [15, 16], Cu(110) [17] and Ru(0001) [18] in dynamical calculations using the molecular dynamics with electronic friction (MDEF) model. These studies have shown that non-adiabatic effects play a small role in these systems. Additionally, due to the large mismatch between the mass of H_2 and the surface atoms, the energy transfer from the molecule to the metal surface should be small and unlikely to influence the scattering results [19–21]. If we neglect the surface atoms DOFs, we only consider the motion of the molecule in its six DOFs on the ground state PES.

1.2.1 The hydrogen molecule

Let us consider the hydrogen molecule in the gas phase and solve the Schrödinger equation. The solutions are labelled with three quantum numbers, ν , j and m_j. The first quantum number, ν defines the vibrational motion of the molecule. The interaction energy between two atoms in the diatomic molecule is shown as a function of the vibrational coordinate, *i.e.*, the internuclear distance r. $r = r_{eq}$ is the equilibrium bond length of the
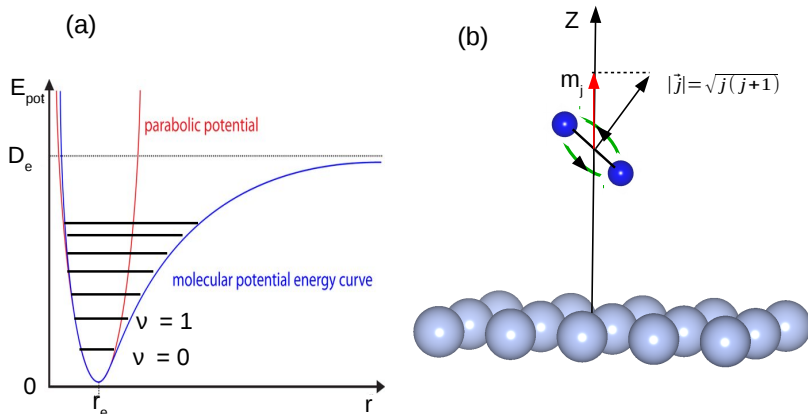
Figure 1.2: (a) Interaction energy curve as a function of molecular bond length for hydrogen molecule. The equilibrium bond length and the dissociative energy are shown as r_e and D_e, respectively. (b) Classical representation of the angular momentum vector $\vec{j}$ of H_2 together with its projection (m_j) on the surface normal (Z), and the definition of its angular momentum quantum number j.

molecule where the energy curve has its minimum. Near the equilibrium position in the potential energy curve, the molecule can be described fairly well by a quadratic equation (as a simple harmonic oscillator). The energy curve increases for both smaller and larger values of r than r_e. For large internuclear distances the interaction energy is close to the dissociation energy. The horizontal lines in Figure 1.2 (a) represent the allowed energy levels associated with the vibrational quantum number. $\nu = 0$ has a particular vibrational energy called the zero-point energy (ZPE) ($E_{\nu_0} = 1/2h\nu$). The rotational motion of the molecule is represented by the next two quantum numbers, j, and m_j. The angular momentum vector $\vec{j}$ together with its projection m_j onto a space-fixed axis (Z) are shown in Figure 1.2 (b) . $\vec{j}$

is oriented perpendicular to the plane of rotation and has a length equal to $\sqrt{j(j+1)}$ in atomic units, where j is an integer number and called the rotational or angular momentum quantum number. The projection of $\vec{j}$ on the surface normal, m_j, the rotational magnetic quantum number can take any integer value between $-j$ and j. Therefore, for a given value of j, there are $2(j+1)$ possible m_j states for a nuclear wave function, which are degenerate. In the rigid rotor approximation the rotational energy of the molecule is given by $\frac{j(j+1)}{2\mu r_e^2}$ in which μ is the reduced mass of the molecule, and is a function of only the quantum number j. In the gas phase, the hydrogen molecule, not only vibrates (associated with one DOF) and rotates (associated with two DOFs) but it also moves translationally in three directions. Therefore, translational motion of the molecule accounts for three of the six molecular DOFs. Molecular translational motion is not quantized. Hence, the molecule can have any amount of initial translational energy with an arbitrary incidence direction.

Hydrogen interacting with a surface

When a hydrogen molecule situated in the gas phase has translational energy towards the metal surface, it will approach the surface and finally interact with the surface. The bond length of the approaching molecule may extend and if the molecule has enough translational or internal energy, it may overcome the barrier to dissociation. The PES of H_2 interacting with a metal surface is not that of a molecule interacting with an ideal flat surface; the corrugation in X and Y can give rise to scattering in or out of the incidence collision plane (See Figure 1.3). During this physical process, the molecule can also transfer (gain) energy to (from) the surface. Based also on this energy transfer we can distinguish the following phenomena:(a) elastic scattering: if no energy is transferred between the molecule and the surface during the collision; (b) vibrationally inelastic scattering: the molecular vibrational energy increases or decreases during the collision, because energy is transferred towards (from) the molecular vibrational motion;(c) rotationally inelastic scattering: the molecular rotational energy increases or decreases during the collision;(d) diffraction or diffractive scattering: the parallel (to the surface) momentum of the molecule near a surface can only change by discrete quantities, due to the periodicity of the surface; as a result the angular distribution of the scattered molecule presents a discrete peaks distribution. The associated quantum numbers are n and m and
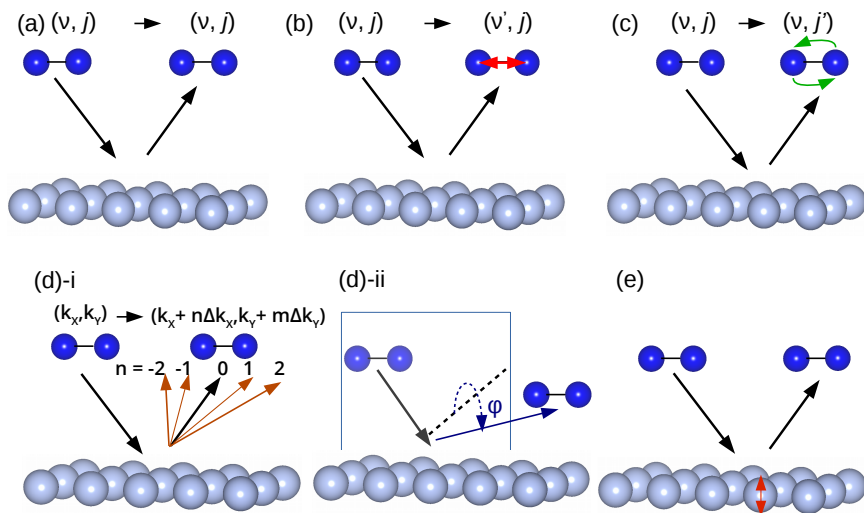
Figure 1.3: Graphical representation of some of the possible outcomes that can happen when a molecule approaches to a surface. (a) elastic scattering, (b) vibrationally inelastic scattering, (c) rotationally inelastic scattering, (d) diffractive scattering (i- in plane, ii- out-of-plane scattering) (e) phonon inelastic scattering.

the diffraction quantum Δk is a surface reciprocal lattice vector and is determined by the periodicity of the direct lattice. For a square surface the diffraction quanta are given by $\Delta k_X = \frac{2\pi}{L_X}$ and $\Delta k_Y = \frac{2\pi}{L_Y}$, where L_X and L_Y are the length of surface unit cell, respectively. There is special case of diffraction called specular scattering or specular reflection when $n = m = 0$. In all these processes, the molecule may also excite surface DOFs, *i.e.*, phonons (surface vibrations) and electron-hole pairs (Figure 1.3 (e)).

The details of the dynamics give us information about the topography of the PES. To study the reaction mechanisms, the reaction barrier height, and the barrier position are very important to classify the dynamics of molecule-surface interactions. The existence or lack of a barrier to dissociation in the most favorable reaction pathway on the PES distinguishes the type of H_2-

metal surface system. Such a system can show activated or non-activated dissociation.

H_2 dissociation is activated on noble metals, examples of activated systems include H_2 dissociation on Cu(111) [22], Cu(110) [22], Cu(100) [22], Ag(111) [23] and Au(111) [23]. These systems show late (close to the surface, long $H-H$ distance), high barriers to dissociation for all possible configurations of the molecule relative to the surface. The reaction probability generally increases as a function of incidence energy monotonically up to saturation value.

Dissociation of H_2 is often non-activated on transition metal surfaces. The systems with non-activated dissociation show no barrier at least in some of the reaction pathways. The other reaction pathways show barriers that can be either early or late. In contrast to the case of direct activated dissociation, in which the reaction probability increases with increasing incidence energy, for lower incidence energies the reaction may also increase with decreasing incidence energy due to trapping of a molecule in a well in the potential. Trapping is only prevalent at low energies when physisorption is important. Examples of non-activated systems include H_2 dissociation on Pd(111) [24], Pd(100) [25], Ni(110) [25], and Ni(100) [25].

There are also systems in between strongly activated and non-activated systems that share properties of both these systems. Examples of these systems are H_2 dissociation on Ru(0001) [26, 27], Pt(111) [14, 28] and Ni(111) [25]. The PES shows only very low barriers to dissociation that often are far away from the surface, *i.e.*, early barriers. The reaction probability curve in these systems is similar to that in highly activated systems, in that reaction increases with increasing incidence energy.

The barrier to dissociation can also change in two different ways when the molecule moves across the surface. Different ways in which the barrier changes give rise to different corrugations of the PES are called energetic corrugation, in which the barrier changes its height, and geometric corrugation, in which the barrier changes its distance to the surface [29, 30]. PES corrugations couple molecular motion parallel and perpendicular to the surface. If there is a specific balance between energetic and geometric corrugation on the surface, it would be expected that dissociation depends only on the component of the incidence energy normal to the surface (normal energy scaling) [30, 31].

Approximations

Unfortunately, it is usually impossible to solve the Schrödinger equation for systems of very high-dimensions. Evidently, some approximations should be made to render the problem tractable. Almost all discussions of chemical reaction dynamics begin with the BO approximation [9]. Under the following circumstances, the validity of the BO approximation holds : (1) the rearrangement of the electron cloud associated with a change of nuclear positions must be gradual; *i.e.*, non-adiabatic coupling must be small; (2) there must be a wide separation in energy between the electronic states of the system; and (3) to permit the electrons to adjust completely their motions, the velocities of the nuclei must be sufficiently small. It can be anticipated that the BO approximation breaks down in molecule-metal surface reactions, because the metal surface exhibits a continuum of electronic states, *i.e.*, there is no energetic gap between electronic states. When a molecule collides with a surface, it can excite electrons on the surface. Electron-hole pair excitation in the electronic levels in the metal can provide a mechanism for energy transfer with an adsorbate molecule, which may cast doubt on the concept of nuclear motion on a PES. Classical mechanical based models which are called friction models have been applied to describe energy transfer between molecular motion and electron-hole pair excitations at metals surfaces [32–34]. One of these methods is called molecular dynamics with electronic friction (MDEF) [34–36], which treats non-adiabatic dynamics at metal surfaces. For H_2 dissociation on Cu(111) [15, 16, 37], Cu(110) [17] and Ru(0001) [18] MDEF has been used to study non-adiabatic effects in dynamical calculations. The studies showed that for H_2 dissociation on metal surfaces, electron-hole pair excitations have a very small effect on reactive and non-reactive scattering, and the BO approximation should work rather well for the reaction of H_2 and D_2 on metal surfaces.

The next approximation is the ideal static surface approximation, in which the surface atoms are fixed and sit in their ideal lattice positions, and as a result, energy exchange between the molecule and the surface atoms and the effect of the increased corrugation of the surface due to surface atom motion are neglected. However, a broadening of the reaction probability curve with surface temperature is found in experiments on H_2 and D_2 desorbing from hot Cu(111) surfaces [38, 39]. *Ab initio* molecular dynamics (AIMD) calculations provide the opportunity to model the effect of surface temperature and surface atom motion on a gas-surface reaction, and have

recently been used to study the dissociation of CH_4 on metal surfaces [40–42]. The study of static surface temperature effects on H_2 dissociation on Cu(111) [43] and AIMD calculations on dissociation of D_2 on Cu(111) [44] showed that the approximation of an ideal static surface works rather well for low surface temperatures, in particular for the simulation of molecular beam experiments for these systems ($T_s = 120$ K).

For many-body systems like a molecule interacting with a metal surface, density functional theory (DFT) is the current method of choice for obtaining an approximate solution to the Schrödinger equation. The central object in DFT is the so-called exchange-correlation (XC) functional. Approximations have to be used to construct the XC functionals, and this affects the accuracy of the description of a molecule-surface reaction. The well-known generalized gradient approximation (GGA) [45, 46] level functionals are commonly used to describe molecule-surface reactions, and these are available in many quantum chemistry software packages. At a lower level than the GGA is the local density approximation (LDA) [47], which does not work well for molecule-surface reactions [48–50]; it yields too low barriers for activated processes compared to experimental data. Further descriptions of the approximation levels for the XC functionals are found in Section 2.2.1.

In order to accurately describe the molecule-surface interaction, a highly accurate PES is required. The PESs obtained from the latest electronic structure theory based on DFT with functionals incorporating a GGA or one step higher level of theory than GGA, *i.e.*, meta-GGA [10, 12, 51] exhibit errors for barrier heights. Furthermore, the long range interaction (van der Waals interaction), which could be important for molecule-metal systems, is not taken into account in common semi-local XC functionals at the GGA level. Recently, a novel implementation of the specific reaction parameter (SRP) approach to DFT, adopted to molecule-surface interactions, was proposed [52]. At present, this methodology is the only DFT approach that has been demonstrated to provide chemically accurate values of barrier heights for reactions of small molecules with metal surfaces. This approach has yielded accurate values of barrier heights for the dissociative chemisorption of H_2 on Cu(111) [52], Cu(100) [53], and Pt(111) [54] and of CHD_3 on Ni(111) [41], Pt(111), and Pt(211) [42]. The SRP−DFT method is semi-empirical, and systematically improves the accuracy of the XC functional by fitting an adjustable parameter in the density functional, such that supersonic molecular beam experiments on the system of interest are reproduced. This method is at the heart of this thesis and it will be

discussed thoroughly in the following chapters.

1.3   Aim of this thesis

As discussed before, one of the main problems in the accurate description of a molecule interacting with a metal surface is the choice of the XC functional used to perform the DFT calculations. In this thesis, the main aim is to provide an improved description of H_2 dissociative chemisorption on metal surfaces based on the semi-empirical SRP method in which the accuracy of XC functionals are systematically improved in a semi-empirical and system specific way, by comparing the experimental data with theoretical results. The goal is to construct a database of reaction barriers with chemical accuracy for H_2 interacting with metal surfaces. The aims of the work reported in the following chapters are briefly summarized here.

- In Chapter 2 the modeling of molecule-surface interactions is described. The basis of the DFT method is described and the SRP method is also briefly explained. The interpolation method used for construction of the PES is given. Finally, the theory of the molecular dynamics methods used in this thesis is represented.

- In Chapter 3, the aim is to extend the development of SRP density functionals, and the database, with a result for a weakly activated dissociative chemisorption reaction of H_2 with a transition metal surface. For this aim, a SRP$-$DF is developed, in which a SRP functional incorporates in the correlation part the revised version of the vdW-DF developed by Lee *et al.* [55] and called vdW-DF2, for the dissociation of dihydrogen on Pt(111) . The study has been performed using semi-empirical density functional theory and the quasi-classical trajectory (QCT) method. The validity of the QCT method is investigated by showing that QCT calculations on reaction of D_2 with Pt(111) closely reproduce quantum dynamics (QD) results for reaction of D_2 in its rovibrational ground state. The goal is to achieve a chemically accurate description of D_2 dissociation on Pt(111) with molecular beam simulations, while reproducing the experimental results at normal and off-normal incidence.

- In Chapter 4, the main focus is on the transferability of an SRP functional among chemically related systems. The SRP functional originally developed to describe chemisorption of dihydrogen on Cu(111) [56] (called SRP48 functional) is tested here on dissociation of the same molecule on Ag(111), with Cu and Ag belonging to the same group of the periodic table. We investigate whether the SRP density functional derived for $H_2 + Cu(111)$ also gives chemically accurate results for $H_2 + Ag(111)$. For this purpose, we performed QCT calculations using the six-dimensional PES of $H_2 + Ag(111)$ within the Born-Oppenheimer static surface (BOSS) approximation. The computed reaction probabilities are compared with both state-resolved associative desorption and molecular beam sticking experiments.

- In Chapter 5, the main goal is to address the question whether the SRP-DF functional derived for $H_2 + Pt(111)$ is transferable to the $H_2 + Pt(211)$ system. Most importantly, the work reported in Chapter 5 also investigates the transferability among systems in which H_2 interacts with different faces of the same transition metal, which is relevant to heterogeneous catalysis.

- In Chapter 6, the focus is on two basic problems of the SRP−DFT methodology. The first problem is that sticking probabilities (to which SRP-DFs functionals are usually fitted) might show differences across experiments, of which the origins are not always clear. The second problem is that it has proven hard to use experiments on diffractive scattering of H_2 from metals for validation purposes, as dynamics calculations using a SRP−DF may yield a rather poor description of the measured data, especially if the potential used contains a van der Waals well.

1.4 Main results

The main results of the work reported in the following chapters are discussed here.

Chapter 3: Chemically Accurate Simulation of Dissociative Chemisorption of D_2 on Pt(111)

In Chapter 3, we obtained an SRP density functional for H_2 + Pt(111) by adjusting the α parameter in the PBEα-vdW-DF2 functional until reaction probabilities computed with the QCT method reproduced sticking probabilities measured for normally incident D_2 with chemical accuracy. We found that using the vdW-DF2 functional improves the description of the molecule-surface interaction compared to the original vdW-DF. Comparison of QD calculations for the initial $(\nu = 0, j = 0)$ state of D_2 with the QCT results establishes the appropriateness of the use of the QCT method. Reproducing the experimental data by using the SRP$-$DF functional and QCT calculations for off-normal incidence for $\theta_i = 30°$ and $45°$, for which computed reaction probabilities show no dependence on the plane of incidence, confirms the quality of the SRP functional. We report that the minimum barrier height obtained for the reaction is -8 meV, in agreement with the experimental observation of no, or only a small energetic threshold to reaction [28]. This value can be entered into a small [8], but growing [41] database with barriers of reactions of molecules with metal surfaces, for which chemical accuracy is claimed.

Chapter 4: Test of the Transferability of the Specific Reaction Parameter Functional for H_2 + Cu(111) to D_2 + Ag(111)

In Chapter 4, we study the transferability of the SRP48 functional, which was initially derived to reproduce experiments for H_2 on Cu(111) with chemical accuracy [56]. In this chapter, we use the QCT method to compute molecular beam sticking probabilities and initial-state resolved reaction probabilities. To establish the appropriateness of the QCT method, we performed the QD calculations for several rovibrational states, and compared with the QCT results. It is found that the QCT reproduces the QD results very well. Results for vibrationally (in)elastic scattering, *i.e.*, probabilities $P(\nu = 2, j = 0 \longrightarrow \nu = \nu')$ as function of incidence energy, are also presented and discussed. It is found that the barrier heights in the SRP48 PES are higher than obtained with the PBE functional as reported by Jiang *et al.* [57]. We also computed molecular beam sticking probabilities and compared with the experimental results of Cottrell *et al.* [58]. The

energy differences between the computed data and the spline interpolated experimental curve were in the range $2 - 2.3$ kcal/mol. Thus, no chemical accuracy was achieved in our theoretical results. Our results show that the SRP48 functional is not transferable to the $H_2 + Ag(111)$ system, although Cu and Ag belong to the same group.

Chapter 5: Transferability of the Specific Reaction Parameter Density Functional for $H_2 + Pt(111)$ to $H_2 + Pt(211)$

In Chapter 5, we study the transferability of the $SRP-DF$ functional which was originally derived for the $H_2 + Pt(111)$ system and is able to reproduce experiments on this system with chemical accuracy. We used the same functional to model the reaction of H_2 on the stepped $Pt(211)$ surface. We have performed molecular beam simulations with the QCT method using the BOSS model. The accuracy of the QCT method was assessed by comparison with QD results for reaction of the ro-vibrational ground state of H_2. The study shows that the theoretical results for sticking of H_2 and D_2 on $Pt(211)$ are in quite good agreement with experiment, but uncertainties remain due to a lack of accuracy of the QCT simulations at low incidence energies, and possible inaccuracies in the reported experimental incidence energies at high energies. We also investigate the non-adiabatic effect of electron-hole pair excitation on the reactivity using the MDEF method, employing the local density friction approximation (LDFA). Only small effects of electron-hole pair excitation on sticking are found.

Chapter 6: Assessment of Two Problems of Specific Reaction Parameter Density Functional Theory : Sticking and Diffraction of H_2 on $Pt(111)$

In Chapter 6, we study two problems faced by the $SRP-DFT$ approach. To address the first problem of the $SRP-DFT$ approach, we have simulated three sets of measurements of sticking probabilities available for $D_2 + Pt(111)$, using four different sets of molecular beam parameters. We compared these experiments on a one-to-one basis. We report that substantial differences exist between the three sticking probability curves measured for $D_2 + Pt(111)$. We discuss the origin of the discrepancies between different experimental data and report the mean absolute deviations between

the data of the experiments. We use four different sets of molecular beam parameters to simulate molecular beam sticking probabilities. Theoretical results for different sets of parameters are compared with available experimental data, and the agreement (disagreement) of theory with experiments is discussed and shown in this chapter. We also discuss the question of which set of beam parameters can best be used to simulate a particular set of molecular beam experiments. We obtained that all three sets of experiments can be described with chemical accuracy using molecular beam parameters describing seeded molecular beams that are broad in energy. Performing simulations with different sets of molecular beam parameters also provide insight into under which conditions the experiments should agree with one another.

To address the second problem of the SRP−DFT approach, we performed diffractive scattering calculations comparing with experiments, using the SRP−DF. The theoretical results are shown and compared with experimental results for off-normal incidence for two incidence directions. Our results show that there are both quantitative and qualitative discrepancies between theory and experiments. Our study suggests that the SRP−DF for H_2 + Pt(111) may not yet be accurate enough to describe the diffraction in this system. The van der Waals well plays a role in the description of scattering of H_2 from Pt(111) surface and with the use of a PES exhibiting a van der Waals well, part of the scattering should be indirect. A similar study on H_2 scattering from Ru(0001) [59] has shown that the agreement between experiment and theory with inclusion of a van der Waals well in the PES was improved by assuming a static surface disorder of metal surface. However, our results established that making this assumption will not improve the agreement between theory and experiment in the case of H_2 scattering from Pt(111).

1.5   Outlook

By combining the results of molecular beam experiments and QCT calculations, it has been shown that the SRP functional quantitatively (to within chemical accuracy) reproduces the initial dissociation probabilities for H_2 on Pt(111), and that it is transferable from the flat (111) surface to a stepped (211) surface of the same metal, as show in Chapter 3 and Chapter 5. Several questions still remain open in this thesis, which are

described and discussed in this section.

It is interesting to check the performance of the SRP−DF functional which was derived for the H_2 + Pt(111) system, for other molecule-metal surface systems in order to test the transferability of the functional among the transition metals in the same group of the periodic table that experimental results are available for H_2 + Ni(111) [60], H_2 + Pd(111) [24]. Experimental results are also available for D_2 dissociative chemisorption on Sn/Pt(111) measured by Hodgson and co-workers [61] to investigate the effect of alloying in an unreactive metal, Sn, on the dynamics of D_2 reacting on Pt(111). It is very interesting to test whether the SRP−DF functional can also be successfully applied to H_2 reacting on a Pt surface with a non-reactive metal alloyed into it. Furthermore, it would be worthwhile to investigate whether the SRP−DF functional developed for H_2 + Pt(111) will also allow a chemically accurate description of the experimentally investigated reaction of H_2 on the stepped Pt(533) surface [62], and on a Pt surface poisoned by CO [63].

In order to construct a diverse database of reaction barriers with chemical accuracy for molecules interacting with the transition metal surfaces, it is interesting to develop better functionals for these systems, for example, to develop an SRP functional for the H_2 + Cu(111) system that is also able to describe the H_2 + Ag(111) system quantitatively. Our results for H_2 reacting on Ag(111) based on the SRP−DF functional for H_2 + Cu(111) underestimate available experimental results, as shown in Chapter 4. Therefore, a chemically accurate description of the dissociative chemisorption of D_2 on Ag(111) is not yet obtained with the SRP48 DFT functional. In this case, the SRP−DF was based on GGA XC functionals. Unfortunately, GGA functionals are not good at both describing the molecule-surface interaction accurately, *i.e.*, reaction barrier heights, and metal surfaces, *i.e.* lattice constants and surface energies [64]. There are several questions related to the performance of XC functionals for molecule-surface reactions that are used so far. The performance of higher level DFT calculations based on for example meta-GGA XC functional is not clear yet. Among the computationally efficient semi-local XC functionals, meta-GGA functionals are most accurate and give both a good description of molecule-surface interaction as well as the surface itself [65]. However, it is still unclear how adding a van der Waals correlation by combining vdW-DF or vdW-DF2 correlations with a meta-GGA exchange functional would affect the PES and dynamics of molecule-surface systems. Further studies are necessary to address the

question whether with a meta-GGA functional it would be possible to get a chemically accurate description of the dissociative chemisorption of H_2 on Cu(111) while at the same time giving a better description for the lattice constant of Cu. Additionally, the other open question should be addressed whether with the meta-GGA functional derived for $H_2 + Cu(111)$ it would be possible to describe accurately the dissociative chemisorption of H_2 on and associative desorption from Ag(111).

The ability to accurately describe the molecule-surface interaction is dependent on an understanding of the source of error in the design, evaluation and analysis of the underlying model. In general, it is not yet fully understood how large the error of GGA functionals is for barrier heights of molecule-surface systems. Additionally, it is not fully clear how this inaccuracy leads to errors in dynamical observables, which are our only sources for comparison with experiments. Only for reaction probabilities it is obvious that a too high barrier height will usually result in too low reaction probabilities and *vice versa*. Previous studies have shown that the barrier heights, and also the way in which the barrier height varies with the impact site are highly dependent on the choice of XC functional [66]. However, barrier calculations alone will not give us more information about the reaction mechanism, dynamics calculations are also necessary [11]. According to the hole model [67], the reaction probability reflects the proportion of impact sites and molecular orientations for which the collision energy exceeds the barrier height at the impact sites and molecular orientations. There are reaction paths without or with only very low barriers as well as reaction paths with substantial barriers to dissociation, *i.e.*, the dissociation takes place over a distribution of barriers varying in height [68]. The curvature of the reaction path in the 2D PES, *i.e.* coupling of translational motion along the minimum energy path (MEP) to vibrational motion is also dependent on the choice of the XC functional [11]. It was shown that this coupling is larger for the SRP functional than GGA functional due to the presence of the van der Waals well [42]. A dynamical effect (called bobsled effect [69]) may remove energy from motion along the MEP and convert it to motion away from the MEP, and reduce the reactivity. Vibrational efficacies greater than 1.0, as shown in Chapter 4, can also be explained in this way that the molecule cannot follow the MEP and slides off it [52, 70].

There is a clear need for more complicated dynamical properties in order to investigate more detailed properties of the PES. Rotationally inelastic scattering or diffractive scattering are far more sensitive to subtle details of

DFT-based PESs [71]. However, the agreement for diffractive scattering of H_2 from Pt(111) compared to diffraction probabilities extracted from the measured angular distributions by Nieto *et al.* [14] is clearly not as good as the agreement obtained for the reaction probabilities of the H_2 + Pt(111) system with the SRP−DF functional. There are qualitatively and quantitatively large differences, as shown in Chapter 6. The previous theoretical results by Nieto *et al.* [14], which were based on the use of a GGA functional, demonstrated better agreement with the experiments. The inclusion of van der Waals effects is crucial to properly describe diffraction of H_2 from metal surfaces and the performance of DFT to describe diffraction spectra may rely on the accuracy of the van der Waals functionals used [72, 73].

Also we note that the SRP−DFT method is semi-empirical and the accuracy of the computed results is no better than the accuracy of the underlying experimental data. Therefore, the availability of highly accurate experimental data is essential and lack of accuracy in the experiments limits the possibility for improving semi-empirical method. As shown in Chapter 6, parameters that describe translational energy distributions of molecular beams play roles in accurately calculating the sticking probabilities. These parameters are extracted from experimental time-of-flight (TOF) measurements. It should be noted that errors may be made in the analysis of the TOF measurements. There is a need for measurements of sticking probabilities accompanied by accurate characterization of the molecular beams used.

Moreover, there is no direct way to compare DFT energies to the molecular beam experiments. Instead, intermediate dynamical simulations are necessary. This makes the fitting procedure indirect and can introduce uncertainties due to (the simplified description of) phonon and electron-hole pair excitations in the surface and the (lack of) quantum-classical correspondences. Thus, it is not yet fully clear how much dynamical models and methods contribute to errors and uncertainties. On the side of theory, development of the QD method incorporating the effects of phonons and electron-hole pair excitation would be useful to improve the accuracy in describing the reaction and describing the diffraction. Also, recent quantum Monte-Carlo (QMC) results for H_2 + Cu(111) suggest that in the future it may be possible to put the SRF−DFT approach on an *ab initio* basis by fitting the SRP−DFT to a few points computed with QMC.

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