Highly accurate simulations and benchmarking of molecule-surface reactions

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General Introduction

1.1 Gas-surface reactions

We are surrounded by molecules. These molecules can interact with each other artificially (in the ways arranged by us) or naturally. These chemical interactions are then part of our everyday life. A well known example of a natural reaction of these molecules is the rusting of the metals left outside in a humid environment. An artificial example is the reduction of the toxic exhaust gases from cars by a catalytic converter[1]. Many of these reactions find their application in industry[2]. A well know example is the Haber-Bosch process,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \tag{1.1}$$

used in the synthesis of ammonia which is an important chemical reaction in the production of artificial fertilizer[3] needed for food production. Another example is steam reforming[4],

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO, \tag{1.2}$$

used to produce hydrogen (H_2) and carbon monoxide (CO) gas from methane (CH_4) and steam. These chemical reactions proceed on a catalyst. For example, in the Haber-Bosch reaction, iron or ruthenium is used as a catalyst, whereas for steam reforming, nickel is commonly used as catalyst. Improving these reactions by designing new catalysts, either by allowing cheaper materials to be used as catalysts or by reducing the energy cost of a given reaction, have a potentially huge impact on the chemical industry[5]. Due to the considerable importance of these chemical reactions for industry, it is not surprising that they receive much attention from both theoretical and experimental studies. It is then the job of the chemist to understand why and how these reactions take place, at the experimental level, and also at the theoretical level in order to achieve improvements.

As a simple form of a chemical reaction let us consider two molecules (reactants) coming together with enough energy to overcome the energetic barrier to that reaction and then reacting to form the product(s). During this reaction, bonds are broken, and new bonds are formed. The chemical reaction that takes place in the presence of a catalyst is called a catalyzed reaction. A catalyst is a reaction partner that interacts with the reactants to provide an alternative reaction mechanism that is energetically more favorable. In general, a catalyst stabilizes the transition state of the reaction complex formed by the reactants coming together on a catalyst, thereby lowering the barrier (Fig.1.1) to reaction and facilitating the breaking of existing chemical bonds and the formation of new chemical bonds.

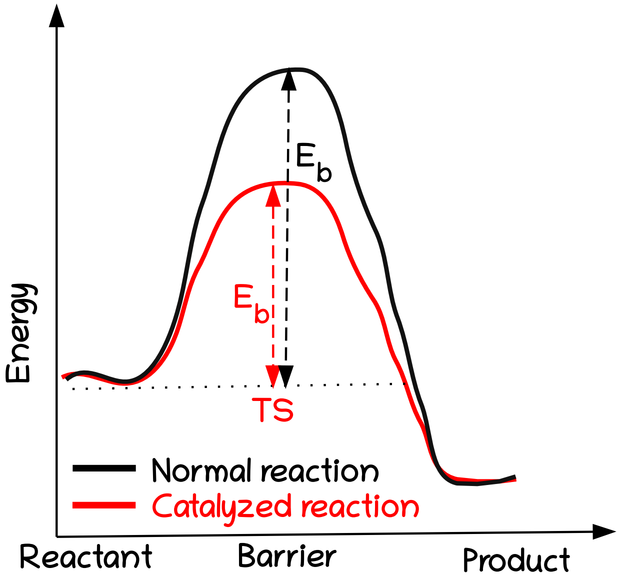

FIGURE 1.1: The schematic overview of the role of the catalyzed reaction.

The products that are formed after the reaction move away from the catalyst, allowing the catalyst to participate in a new catalytic cycle. The catalyst creates an alternative energetic pathway by lowering the energetic barrier to speed the reaction. It increases the reaction rate and may allow it to proceed under milder conditions (lower temperature and or pressure), reducing the cost. In many cases, it is also possible to increase the selectivity of the catalyst such that the formation of a desired reaction product is favored over an unwanted reaction product, reducing waste and pollution. If the reactants and the catalyst exist in distinct phases (plasma, gas, liquid, solid), we call it heterogeneous catalysis, while in homogeneous catalysis both the catalyst and the reactants are in the same phase. Another important type of catalysis that cannot go unmentioned is biocatalysis, in which proteins act as highly specialized catalysts (enzymes) for nearly all biochemical reactions underpinning life as we know it[6].

1.2 Molecule metal-surface reaction mechanisms

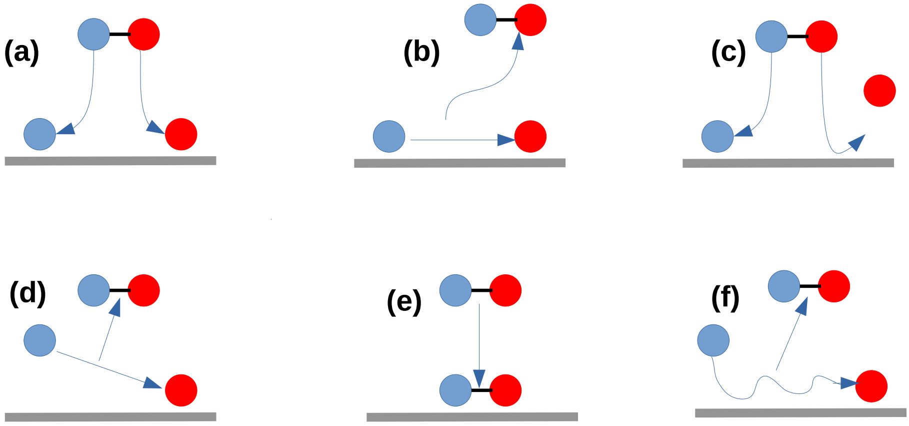

FIGURE 1.2: Schematic overview of different mechanisms for molecule metal-surface reactions. (a) dissociative chemisorption, (b) Langmuir-Hinshelwood reaction, (c) abstraction, (d) Eley-Rideal reaction, (e) molecular adsorption and (f) hot-atom reaction.

When a molecule interacts with a surface, reactions may proceed through several mechanisms, the most common mechanisms being shown in Fig.1.2. Three of these mechanisms involve the adsorption of the reactant molecule to the surface: dissociative chemisorption (DC), in which a bond in the incoming reactant is broken and both fragments are adsorbed to the surface (Fig.1.2.a); abstraction, in which after a bond in the reactant incoming molecule is broken, only one fragment is adsorbed to the surface while the other fragment returns to the gas phase (Fig.1.2.c); and molecular adsorption, in which the whole molecule is adsorbed to the surface, without bond breaking (Fig.1.2.e). This last mechanism can happen through chemisorption or physisorption. Other reaction mechanisms are: the Langmuir-Hinshelwood reaction, in which two atoms and/or molecules that are adsorbed to the surface can combine, form a new bond and the newly formed molecule desorbs (Fig.1.2.b); Eley-Rideal reaction, in which one atom/or molecule coming from the gas phase reacts directly with an adsorbed atom/or molecule on the surface and the newly formed molecule directly desorbs from the surface (Fig.1.2.d); and Fig.1.2.f the hot-atom reaction, in which a molecule coming from the gas phase is temporarily trapped and bounces on the surface not achieving thermal equilibrium with it, and collides with another molecule adsorbed on the surface to form a bond, and the newly molecule formed desorbs. In 2007 Ertl was awarded the Nobel prize in chemistry for investigating elementary reaction steps in heterogeneous catalysis experimentally[7].

In many cases DC is the rate-limiting step in a heterogeneously catalyzed process[8,9]. Creating a theoretical description of a complex reaction network ideally starts with the calculation of 'chemically accurate' barrier heights for such elementary reaction steps[10]. Calculating chemically accurate barrier heights for rate-controlling reactions to obtain accurate rates of the overall reaction network[11] is a complex task. This task not only needs to take into account the static electronic structures of both the reactant and the catalytic surface at the transition state, but often also dynamical effects such as the molecule's approach towards the transition state, the molecule's internal motion, as well as surface atom motion due to temperature[12].

1.3 Background to topics of this thesis

1.3.1 H_2 reacting on metal surfaces

As mentioned in the previous section, DC is often a rate-limiting step in heterogeneously catalyzed process. From a fundamental point of view, understanding how a molecule reacts on a surface is helped by investigating how the simplest molecule (hydrogen) dissociates on a clean metal surface with a well-defined structure. Also, the dissociation of hydrogen is relevant to the industry. It is used in the synthesis of methanol from CO_2 over a $Cu/ZnO/Al_2O_3$ catalyst, in which process the dissociation of hydrogen is considered to be an important step[13–15]. Another reaction that has an extensive use in the chemical industry[16–21] is the hydrogenation of unsaturated bonds in organic molecules through heterogeneous catalysis on solids.

The DC of hydrogen on metal surfaces has served as an ideal model system. It has been the subject of many theoretical and experimental studies. Experiments carried out in the ultra-high vacuum (UHV) have been used to study the dynamics of hydrogen dissociation, recombinative desorption, and scattering[22–59]. However, there is still a lot to do about the dynamics and kinetics of H_2 dissociation at industrially relevant temperatures and pressures[60,61].

Experiments on the reaction scattering of H_2 from metal surfaces, have investigated a wealth of phenomena. Sticking probability versus collision energy curves can be obtained directly from molecular beam experiments[23,24,29,36,39–41,48–52,62] or indirectly from associative desorption experiments[23,25,29,38,63] if detailed balance is assumed. From associative desorption experiments, we can derive information on the effect of the initial rovibrational state[23,25,29,38,63], and also of the alignment of the molecule relative to the surface on the reverse DC reaction[27]. From state-resolved molecular beam experiments in which H_2 scatters from a surface, information on vibrational excitation[31], rotationally elastic[22] and inelastic[32] scattering, and vibrationally and rotationally inelastic scattering[33,54] can be obtained. Elastic and inelastic diffractive scattering of H_2 from metal surfaces can be assessed as well[55–59,64–68].

Using molecular beam techniques, the sticking probability can be measured directly using the King and Wells method[69]. In this technique, a gas (molecular beam) is collimated by skimmers, then supersonically expands into a UHV chamber toward the target surface. The initial pressure in the UHV chamber drops when the molecular beam entering the chamber interacts with the surface and molecules stick, and rises when the molecular beam entering the chamber does not react with the surface. The sticking probability can be obtained from the differences in the pressures measured.

Associative desorption[25,29,38,42,43,63,70–72] is another experimental technique where the potential energy surface of the molecule interacting with the surface can be explored. In this approach, resonance-enhanced multi-photon ionization[23,25,29,38,63] (REMPI) can be used to obtain information on state-specific reaction.

One of the biggest challenges to theorists is to help with understanding and improving the above experiments. Theoretically, to understand, control, and predict the rate of heterogeneously catalyzed processes, the DC of a molecule on a metal surface has been widely studied[73–90]. Typically density functional theory (DFT[91,92]) has been used. Some of the research focused on improving on existing exchange-correlation (XC) functionals. One example concernes the specific reaction parameter approach to density functional theory (SRP-DFT)[79] for dissociative chemisorption on metal surfaces, which has enabled achieving chemical accuracy for several systems[63,79,80,87,93–95]. In some cases, transferability of the SRP density functional (SRP-DF) among chemically similar systems has been found[96–98].

To accurately simulate the experimental sticking coefficients (S_0), many points have to be considered. In general, the product of the reaction between a molecule and a metal surface is influenced by the details of the interaction potential between the molecule and the surface. Many factors can play a role during the approach of a gas phase molecule to the surface. Firstly, due to their thermal motion, the surface atoms can be displaced from their equilibrium positions. As a consequence, the interaction potential between molecule and surface might be modified. Secondly, due to the vibrational coupling with the phonons of the lattice, there can be energy exchange between the molecule and the surface. Finally, electron-hole pair excitation (a non-adiabatic effect) due to the transfer of a small amount of energy from molecular motion to electrons lying just below the Fermi level might also influence the reaction dynamics. The role played by surface temperature, surface atom motion, and non-adiabatic effects might differ from system to system.

In the literature, many studies have taken into account these processes. For example, electron-hole (e-h) pair excitation has been taken into account in the study of H_2 scattering from Pt(111). This study suggested that e-h pair excitation should not play a large role[66] in this system, as both reaction and diffraction could be well described with one and the same potential energy surface. Non-adiabatic effects have been taken into account directly in the study of H_2 dissociating on Cu(111)[99,100], Cu(110)[101] and Ru(0001)[102] using electron friction models. From these studies, no large non-adiabatic effects have been found, suggesting that e-h pair excitation does not play a significant role for H_2 interacting with metals. In addition, because of the large mass mismatch between the H_2 molecule and a surface atom[103,104], for activated systems, the amount of energy exchanged between H_2 and the surface atoms is not expected to be large[12,105,106]. For the thermal motion, a density functional molecular dynamics (DFMD) study of D_2 on Cu(111)[80] has revealed that for low surface temperatures (T_s=120K) the Born-Oppenheimer static surface (BOSS) model works quite well.

In view of the above, it becomes computationally feasible to map out a potential energy surface in six dimensions (6D), for H_2 interacting with a metal surface, and use it to compute accurate molecular beam sticking probabilities (or DC probabilities) using the (quasi-)classical trajectory method or quantum dynamics.

1.3.2 Databases

In general, accurate barrier heights are key to understanding, controlling, and predicting chemical reactions. Our ability to understand and predict heterogeneous catalysis could be increased if there would exist accurate databases of barrier heights for molecule-metal surface reactions.

While databases exist for gas phase reactions[107–110] and for reaction energies on metal surfaces[111–113], they are scarce for barriers to DC on metals. For adsorption bond energies to transition metal surface, for example, a database was recently built which contains data for 39 systems[113]. This database was used to test several density functionals[111–117] and has been extended so that it now contains[118] data for 81 systems.

The first database (CatApp[119,120]) on barrier heights for DC was built using only one DF (RPBE[121]). A more recent database on DC is the SBH10[122] database containing results for 10 systems and benchmarked with the 2^{nd} rung BEEF-vdW2[111], 3^{rd} rung MS2[123] and 4^{th} rung HSE06[124] DF of Jacob's ladder[125,126]. Why are databases for barrier heights for DC scarce?

One of the main reasons has been that, until very recently, only DFT could be used to study DC on metals, which is less accurate. Therefore, until recently it was not well known how large the errors are in barrier heights when using semi-local XC functionals. Some indication in the literature can be found about the performance of semi-local functionals for gas phase reactions. A test on the BH206[108] database using the MN12-L[127] and N12[128] showed root-mean square deviations of 4.3 and 7.1 kcal/mol, respectively, which is still far from the chemical accuracy standard (1 kcal/mol). Very recently, the use of SRP-DFT (a semi-empirical method) has enabled a description of barrier heights for several DC systems (14) with chemical accuracy[129]. This suggests the construction of a new database for DC on metals, as discussed below.

1.3.3 Mixed DFs for SRP-DF development

As mentioned in the above subsection, the SRP-DFT approach has already allowed the construction of a small database (SRP14) containing 14 systems for molecule-metal surface reactions[129]. But there is still a conundrum at the heart of this approach, in particular about how to mix exchange and correlation DFs at the general gradient approximation (GGA) or meta-GGA level of theory to DFT to enable one to accurately reproduce barrier heights for DC. Several ways of mixing functionals can be found in literature: (i) using a weighted average of two exchange correlation (XC) functionals within the GGA[63,79], (ii) using a weighted average of two exchange (X) functionals within the GGA and to combine the resulting X functional with a GGA correlation (C) functional[80], (iii) as in (ii), but using a non-local C functional[96,130–132] also approximately describing the attractive van der Waals interaction[133,134], (iv) by the use of a GGA exchange functional that was designed to be tunable[135] and by combining it with non-local van der Waals correlation[95,136], and (v) by the use of meta-GGA functionals either with semi-local correlation[137] or in combination with non-local correlation[87]. An interesting question is whether a general expression of a mixed DF can be found that will allow one to reproduce the barrier for DC on metals for any system.

1.4 Aims of this thesis

The main goals of the thesis are to improve the theoretical description of reactive scattering of H_2 from various transition metal surfaces, such as Ni(111) and Al(110), to build a database with barrier heights for DC to allow testing of electronic structure methods and to develop a more general expression of a mixed DF that can function as an SRP-DF for any DC-on-metal-surface system. For the two H_2-metal systems mentioned, we would like to reduce the bridge between theory and experiment regarding the description of reaction dynamics, through the design of accurate SRP-DFs. Furthermore, the explosion of computational studies in heterogeneous catalysis on metal surfaces has raised the question how reliable existing density functionals are. Therefore, there is a need for benchmark data sets. For this, we take a first step to build a database for barrier heights to DC. We also investigate several expressions of mixed DFs for their ability to function as SRP functionals, with the idea of deriving an SRP-DF that can work for all or most systems with a charge transfer energy greater than 7 eV. Here, the charge transfer energy is defined as the difference of the work function of the metal surface and the electron affinity of the molecule.

All the theories behind this thesis are discussed directly in the following **Chapters**. The **Chapters** in this thesis address the aims mentioned above as follows:

In Chapter 2, we aim to develop an entry to the database of chemically accurate barriers for DC on metal surfaces, i.e., the barrier height for DC of H_2 on Ni(111), for which several molecular beam experiments exist. New potential energy surfaces for this system were computed at the GGA and the GGA + vdW level of theory using various density functionals. The PESs were used to evaluate sticking coefficients and reaction probabilities using the quasi-classical trajectory and the time-dependent wave packet method. The theoretical results obtained were then compared to experimental measurements, and an SRP DF and a chemically accurate barrier height were derived.

In Chapter 3, the aim is to present an extended database for the DC of molecules on metal surfaces, which can be used for benchmarking purposes. In our approach we avoid an important flaw from the previous SBH10 database[122], in which transition states were modeled incorrectly by allowing the metal surface to relax in the molecule's presence. We introduce a new concept of algorithms (light, medium and higher). We tested these three algorithms and 14 density functionals on the database, which can now be used by other electronic structure theorists to test their approaches to DC on metals.

In Chapter 4 the focus lies on the highly activated DC of H_2 on Al(110). The goal is to establish whether the dynamics in this highly activated system can still be accurately described by the quasi-classical trajectory method. To answer this question, we performed dynamics calculations on a potential energy surface computed with a first principles based SRP density functional that has been fitted to recent diffusion Monte-Carlo calculations. Quantum dynamics (QD) and quasi-classical trajectory (QCT) calculations are used to compute sticking probabilities. A detailed comparison between QD and QCT calculations elucidates the importance of quantum effects on the DC in this highly activated system.

In Chapter 5 the focus lies on a basic principle on how density functionals at the GGA and GGA +vdW levels can be mixed to construct an SRP DF that will reproduce with accuracy barrier heights for DC of molecules on metal surfaces. For this purpose, we tested 7 expressions of mixed DFs on a database with 16 entries we called SBH16 (the SBH17 database of **Chapter 3** with H_2+Pt(211) removed) using the medium algorithm method introduced in **Chapter 3**. We also investigated in this chapter how the amount of the RPBE exchange in an SRP DF correlates with the charge-transfer energy, which is defined as the difference of the work function of the metal surface and the electron affinity of the molecule.

1.5 Main results

The main results obtained in this thesis are summarized here.

In **Chapter 2**, we develop a SRP-DF for H_2 on Ni(111), also investigating if the SRP-DF derived previously for H_2+Pt(111)[136] is transferable to the system investigated. To address these questions, 6D PESs have been constructed for the dissociation of H_2+Ni(111) using nine different exchange-correlation functionals. The PESs calculated were then interpolated using the CRP method. To compare with experimentally measured sticking probabilities, quasi-classical trajectory and quantum dynamics calculations have been performed using the BOSS model.

The functionals investigated have shown that DFs with van der Waals correlation yield barriers closer to the surface and exhibit larger energetic corrugation than those with PBE correlation. The PBE-vdW-DF2 and RPBE:PBE(50:50)vdW-DF1 functionals describe the sticking experiments[62] performed by the Rendulic group quite well, with PBE-vdW-DF2 giving the best results. From the comparison with the most recent molecular beam experiments[51] performed by the

Rendulic group, we conclude that PBE-vdW-DF2 can be considered to be a candidate SRP-DF for H_2 + Ni(111). However, the PBEα=0.57-vdW-DF2 functional, which is a SRP-DF for H_2 on Pt(111) is not transferable to H_2 + Ni(111), even though Ni and Pt belong to the same group.

Even if the PBE-vdW-DF2 is considered as a candidate SRP-DF for H_2 + Ni(111), the sticking probabilities obtained for this DF are not yet in good agreement with the experiments of the Rendulic group[51] for incidence energies > 0.25 eV. We found that for incidence energies > 0.25 eV, S_0 starts to exhibit a considerable dependence on the beam conditions, so that some of the discrepancies noted could be due to different beam parameters characterizing the experimental beams and the beams simulated in the calculations. Other possible causes of error in the experiments have also been discussed.

In **Chapter 3** we present a new database with barrier heights for DC on metal surfaces that can be used for benchmarking electronic structure methods. The new database is called SBH17 and contains barriers for 17 systems, including 8 H_2 metal systems, 2 N_2 metal systems, and 7 CH_4 metal systems. For 16 systems the work function of the metal surface minus the electron affinity of the molecule exceeds 7 eV. The barrier heights come from SRP-DFT (14 systems) and from estimates derived using more ad hoc semi-empirical methods (3 systems). The new database is meant to replace an older database (SBH10) that contained barriers for 10 of the 17 systems now treated.

We have tested 14 DFs on the new database, of which three were GGA DFs, 4 meta-GGA DFs and 7 DFs contained GGA exchange and vdW-DF1 or vdW -DF2 non-local correlation. Three different algorithms were tested, which were labeled "high", "medium" and "light" according to the investment of computer time that was required for the calculation.

Of the DFs tested, the meta-GGA DFs perform best at describing the metal, followed by PBE and optPBE-DF1. When the MAE is taken as the accuracy criterion, the workhorse PBE GGA DF performs best on the SBH17 database, with a MAE of 2.4 kcal/mol. Other top performers are the MS2 meta-GGA functional and two functionals consisting of GGA exchange and non-local correlation (SRP32-vdW-DF1 and PBEα57-vdW-DF2). None of the DFs tested systematically underestimates reaction barriers for DC on metals, in contrast to findings for gas phase reactions. We obtain different results regarding the relative accuracy of the MS2 and BEEF-vdW-DF2 functionals than obtained in an earlier study of the SBH10 database, which we attribute to an incorrect treatment of the surface atoms in the transition states in the earlier study.

For the sub-databases with H_2-metal systems, N_2-metal systems, and CH_4-metal systems, rankings are obtained that differ from the overall ranking for the complete database. The SRP50-DF (the 50/50 mixture of the PBE and RPBE GGA DFs) performs best for H_2-metal systems. BEEF-vdW-DF2 performs best for N_2-metal systems, and SRP32-vdW-DF1 for CH_4-metal systems.

The DFs performing best for DC barriers (i.e., kinetics) are not the ones that perform best for databases[112,138] (CE26, CE21b) of chemisorption energies on metals (i.e., thermochemistry). This trend is paralleled in the performance of DFs on databases for kinetics (BH76, BH206) and thermochemistry (AE6, TCE) in the gas phase. The meta-GGA MS2 DF is the functional with the best overall performance for DC barriers and chemisorption energies on metals. Of the five GGA and meta-GGA DFs considered for their performance on 6 databases for kinetics and thermochemistry on metal surfaces and in the gas phase (PBE, RPBE, revTPSS, MS2, and SCAN) again MS2 showed the best overall performance.

In **Chapter 4** we evaluate the accuracy of the QCT method, or, alternatively, the importance of quantum effects for the sticking of H_2 on Al(110), for conditions that should be close to the conditions under which molecular beam experiments have been done on this system[139]. For this purpose, QCT and QD calculations have been done with the BOSS model on a PES obtained with DFT, which exhibits a minimum barrier height close to that recently obtained with QMC calculations[140]. To keep the number of QD calculations to be performed small, a procedure was used in which Monte-Carlo averaging over the initial rovibrational states of H_2 was employed. This procedure allowed the quasi-classical calculation of sticking probabilities with a relative error $< 7.5\%$ for 5 of the six initial conditions investigated, and of 16% for one of these conditions, at approximately an order of magnitude less computation time.

The sticking probabilities computed with QD using the PMC procedure exceed the ones computed with the QCT method by 80 and 30% for the two beam conditions corresponding to the lowest average incidence energies (5.1 and 6.0 kcal/mol), decreasing to only 5% for the highest incidence energy of 9.4 kcal/mol. The sticking probability curve computed with QD is shifted to lower energies relative to the QCT curve by 0.21 to 0.05 kcal/mol, with the highest shift obtained for the lowest incidence energy.

These "quantum effects" may be viewed as being rather small for molecular beam sticking experiments in which the average incidence energies (5.1-8.5 kcal/mol) are much smaller than the minimum barrier height of the system investigated (24.8 kcal/mol). The smallness of the quantum effects is explained on the basis of the large vibrational efficacy of the system (> 1 for $\nu=1$) and of the broadness of the translational energy distributions of the molecular beams used in the experiments we address.

Finally, in **Chapter 5** we have investigated the tunability of several expressions for mixed density functionals, in which a mixing parameter $\boldsymbol{x}$ can be tuned to enable the mixed DF to reproduce the reference value of the barrier height to DC of a molecule on a metal surface. The mixed functionals are tested on the barriers collected in the database we call SBH16, which is equal to the previously reported SBH17 database of **Chapter 3** with the H_2 + Pt(211) system removed from it.

Several finding are reported. Increasing the fraction of RPBE exchange incorporated in the mixed DFs leads to higher barriers. In addition, all mixed DFs tested are well tunable towards higher barriers, as their limiting forms (RPBE, RPBE-vdW1, and RPBE-vdW2) all systematically overestimate the barrier height for the systems in the SBH16 database. Furthermore, the mixed SRP$\boldsymbol{x}$sol-vdW2 DF could describe the minimum barrier height of 15 of the 16 systems using vdW-DF2 correlation, while the mixed SRP$\boldsymbol{x}$-vdW1 DF could do so for 14 of the 16 systems using vdW-DF1 correlation. The mixed SRP$\boldsymbol{x}$sol GGA DF could describe the minimum barrier height of all 16 systems tested.

Finally, we also tested whether and how the mixing coefficient of the mixed DFs is correlated with the charge transfer parameter describing the system, i.e., the difference between the work function of the metal surface and the electron affinity of the molecule. The answer depends on which mixed DF is used. For the SRP$\boldsymbol{x}$ and SRP$\boldsymbol{x}$sol DFs, which both use PBE correlation, we found that the optimum fraction of RPBE exchange decreases with the charge transfer parameter, as could be expected on the basis of earlier results. However, the opposite relationship and weaker correlation was found for the mixed DFs using vdW-DF1 or vdW-DF2 correlation.

1.6 Outlook

All the questions that remain open with regard to the results that we have presented in this thesis are discussed in this Section, as well as the potential future investigations this research opens the door to.

The development of the SRP-DFs that can describe the reaction of a molecule with multiple transition metal surfaces to within chemical accuracy is still not yet clear. From the previous work of the DC of the H_2 on Pt(111)[136], it was suggested that the functional that allowed to achieve chemical accuracy for that system could also be transferable to H_2 on Ni(111). The results presented in **Chapter 2** show that the SRP-DF for H_2 on Pt(111)[136] is not an SRP-DF for H_2 on Ni(111) even though Ni and Pt belong to the same group in the periodic table. In contrast to this finding, the previous SRP-DF developed for CH_4 on Ni(111)[131] was found to be an SRP-DF for several other CH_4-metal systems[93,96,98,129,141]. Why is the SRP-DF developed for CH_4+Ni(111) transferable to CH_4+Pt(111), while the SRP-DF for H_2 on Pt(111) is not transferable to H_2+Ni(111)? This question is difficult to answer and remains open. Further studies are necessary to establish, for instance, whether the transferability depends on the nature of the mixed DF that is parameterized.

The ability to describe with accuracy the DC of a molecule on metal surfaces does not only depend on the performance of the parameterized mixed DF used, but also on the availability of highly accurate experimental data. The theoretical sticking probabilities obtained for H_2 on Ni(111) are not yet in good agreement with the experiment[62]. As discussed in **Chapter 2**, these discrepancies can perhaps be attributed to differences between the beam parameters that characterize the experiment and the beam parameters used for simulations. The comparison of different sets of experimental sticking coefficients also shows multiple discrepancies. To resolve this, the availability of highly accurate and well-defined experimental data is of great importance, and it would be good if new and accurate results would become available for H_2 on Ni(111).

The results for DC of H_2 on Cu(111)[142], Cu(211)[85], Ru(0001)[130] and also the results presented in **Chapter 2** suggest that quantum effects are not of large importance to DC of H_2 on metals. The sticking probability curve computed with quantum dynamics in **Chapter 4** for H_2 reacting on Al(110) is shifted to lower energies relative to the quasi-classical curve by 0.21 to 0.05 kcal/mol. This result shows that the quantum effects are also not very important for this highly activated system. This raises an important question. How important are quantum effects on the DC for highly activated H_2-metal systems really since we know the H_2 on Al(110) system has a minimum barrier height $>$ 1 eV? It will be worthwhile to also investigate whether the observation that quantum effects are not very important also holds for other systems with minimum barriers higher than 1 eV such as H_2 on Ag(111)[87,142,143] and Au(111)[142–144].

On the basis of the results presented in **Chapter 3**, we see the following possible improvements of the present database for DC barriers on metals, and for testing DFs on the database.

First, we suggest that in future the entries in the database are as much as possible based on SRP-DFT, and not on more ad-hoc SE procedures. This would require dynamics calculations with trial DFs on CH_4 + Ru(0001) and CH_4 + Ni(100), for which molecular beam experiments are already available[145,146], and new experiments and dynamics calculations on N_2 + Ru($10\bar{1}0$), for which molecular beam sticking experiments are, to our knowledge, not yet available. As noted above our comparison between MAEs computed with PBE for SBH17 and SBH14-SRP suggests that replacing the reference values with SRP-DFT values for the three systems mentioned is likely to lead to smaller MAEs for a thus improved version of the SBH17 database. Second, we suggest that the database be extended with additional N_2-metal systems. It may be possible to do this by semi-empirically fitting SRP-DFs to supersonic molecular beam sticking data on N_2 + Fe(111)[147,148], W(110)[149,150], and W(100)[150–153]. Adding these data is desirable to make the database more balanced, as it is now dominated by data for DC of H_2 and CH_4 on metal surfaces. Also, it would show whether our results for the MS2 DF are robust to addition of more N_2-metal systems to the database, for which this DF did not perform so well, and the same holds for the optPBE-vdW-DF1 and PBE DFs.

On the longer term, it should be necessary to extend the database with systems for which the charge transfer energy, which equals (WF-EA), where WF is the work function of the metal surface and EA the electron affinity of the molecule, is less than 7 eV. As noted in Ref.[154], DFs with semi-local exchange would appear to systematically overestimate the reactivity of such systems, suggesting that DFs with screened exact exchange are required for a good description. Examples of systems for which molecular beam sticking data are available include e.g. H_2O + Ni(111)[155], HCl + Au(111)[156], and O_2 + Al(111)[157,158], Ag(110)[159,160], Cu(100)[161], and Cu(111)[162]. Inclusion of such systems in the database would certainly alter the view of the performance of DFs for DC on metal surfaces, where the view offered in the present work is specific to systems with (WF-EA) > 7 eV, the only exception being N_2 + Ru($10\bar{1}0$).

Finally, a far larger number of DFs exists than we tested. While we could mention specific DFs here that would be nice to test, this might not do justice to others, as several DFs exist (see e.g. the DFs tested in Refs.[107,108,110]). However, a particular DF we would like to mention is the new machine learned DF DM21[163]. Even though this DF has not been trained on interactions involving transition metals, it would be good to see how it performs on SBH17. It would also be good to test recently developed functionals combining screened exact exchange with vdW-DF1 and vdW-DF2 correlation[164,165], which may work especially well for the representative database we envisage. We advocate that such future benchmark tests would also incorporate calculations employing the CE26 database for chemisorption on metals[112].

Finally, for **Chapter 5**, the results presented have opened the door to several new lines of research. First of all the results underscore the need to obtain better reference values for the H_2 + Ag(111), CH_4 + Ru(0001), and CH_4 + Ni(100) systems. For all mixed DFs the optimized mixing coefficients for these systems appear as outliers when plotted as a function of the charge transfer parameter, and removing these systems from the database leads to correlation coefficients with an increased absolute value for the mixed SRP$\boldsymbol{x}$ and SRP$\boldsymbol{x}$sol DFs for the

H_2-metal surface and the CH_4-metal surface systems.

A small improvement over using the SRP$\boldsymbol{x}$sol mixed DF could be to use a DF that simply mixes the RPBE and the PBEsol exchange-correlation functionals. This would avoid the use of an exchange correlation functional with unbalanced exchange and correlation at the lower $\boldsymbol{x}$=0 end of the spectrum, i.e., PBEsolc.

When it comes to designing mixed functionals incorporating vdW-DF1 or vdW-DF2 correlation, another idea worth testing might be to investigate mixtures of weakly repulsive GGA exchange DFs that are appropriate matches for the vdW1 and vdW2 correlation functionals with the rather repulsive[165] exchange functionals combined with these C functionals in the original vdW-DF1[133] and vdW-DF2[134] DFs. Examples of such exchange functionals have been incorporated in the C09[166] and CX[167] vdW functionals, and other exchange functionals mentioned in Ref.[165]. Another idea would be to explore mixtures of repulsive meta-GGA DFs (such as MS-B86bl[137]) and attractive meta-GGA DFs (such as SCAN[168]) that tend to overestimate respectively underestimate barriers to DC of molecules on metals[169]. It would also be of interest to investigate the performance of mixtures of, or parameterized forms of screened hybrid functionals such as HSE06[124] and screened functionals incorporating van der Waals correlation[164,165]. However, it might be most productive to test such hybrid functionals once a database becomes available that also incorporates good reference values of barrier heights for systems characterized by charge transfer parameters < 7 eV, such as O_2 + Ag(111)[154] and HCl + Au(111)[156]. Such systems presently defy an accurate description based on DFs incorporating GGA exchange[154,156,170].

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