Accurate modeling of the dynamics of dissociative chemisorption on metal surfaces

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Citation

Gerrits, N. (2021, September 23). *Accurate modeling of the dynamics of dissociative chemisorption on metal surfaces*. Retrieved from https://hdl.handle.net/1887/3213516

Chapter 1

General Introduction

1.1 Heterogeneous Catalysis

Catalysis plays an extremely important role in chemistry: Catalysts alter reaction pathways by, e.g., stabilizing reaction intermediates and changing barrier heights. This way, different (milder) reaction conditions and a considerable selectivity towards the desired products can be achieved. Thus, many chemicals can be produced efficiently, which would have been impossible without catalysis. For example, the Haber-Bosch process has been instrumental in feeding a large part of the world population and is responsible for the population explosion[1]. In order to improve sustainability, better catalysts are needed, for which fundamental understanding of the working of catalysts is instrumental.

An important subclass of catalysis is heterogeneous catalysis. Here, two different phases can be distinguished for the catalyst and reactants. Typically, a solid catalyst interacts with reactants in the gas or liquid phase. Such a catalyst is not only able to lower barrier heights for bond-breaking, but also involves kinetic effects such as diffusion of reaction intermediates[2], making heterogeneously catalyzed processes complex multi-step processes with multiple possible reaction outcomes. Fortunately, such processes are often rate-controlled by only one or a few states[3–5], which ensures that fundamental research only has to focus on a few reaction steps. However, at the industrial level, heterogeneous catalysts are also structurally complex due to varying sizes and shapes of the catalytic nanoparticles involved. As a result, many different facets are available, which exhibit different elementary reaction rates. Similar to a rate-controlling state, often only a single or a few facets, or edges, dominate the reaction[6]. Therefore, research is often limited to the reaction of molecules on surfaces with specific Miller indices, although this does exclude diffusion effects between different facets. Another aspect to industrial heterogeneous catalysis is the high pressure involved. The high surface density of molecules that may results complicates the extrapolation of experiments and is at present extremely hard, if not intractable, to model at an atomistic level. Thus, fundamental research tends to be performed for reactions in an ultra-high vacuum (i.e., a low pressure), which allows for a relatively straightforward investigation of elementary reaction steps[7]. These aforementioned complexities and their pragmatic solutions also outline the type of research (i.e., surface science) presented in this thesis: Simulations are performed for single molecules reacting on or scattering from well-defined metal surfaces in order to understand reaction mechanisms relevant for heterogeneous catalysis.

1.2 Molecule-Metal Surface Reactions

Although reactive scattering of molecules from well-defined metal surfaces in UHV is considerably less complex than reactions of molecules on nanoparticles under heterogeneous catalytic conditions, the former topic still presents major challenges, both from a theoretical and an experimental point of view. In experiments, typically a well-defined molecular beam (MB), of which the velocity and the rovibrational state distribution are characterized, is directed toward a metal crystal. Thermal rate experiments are possible as well, but are less well-defined than MB studies[8] and are therefore not the focus in this thesis. The characteristics of the MB can be altered via the nozzle temperature and the seeding gas mixture. The nozzle, through which the MB is produced, and its temperature have an effect on the translational, vibrational, and rotational temperatures. Control over only the translational energy can also be achieved by altering the seeding gas mixture. If a heavy molecule is mixed with a light, often inert gas, a considerably higher translational energy can be achieved than by increasing the nozzle temperature, while the rovibrational temperatures are (by approximation) unaffected. Obviously, with a heavy seeding gas the opposite effect for the translational energy is achieved.

The incidence angle of the MB with respect to the surface normal can also be used to control the incidence energy normal to the surface. This is especially useful if normal energy scaling (NES)[9] holds, i.e., if the reaction probability only depends on the molecule's translational energy normal to the surface. Moreover, the rovibrational state population in an MB can be altered not only via the nozzle temperature, but also via state-selective excitation with laser pumping. Also, the alignment of many molecules relative to the surface can be controlled by employing a magnetic field[10] or polarized laser light[11, 12].

So far, only ways of controlling the molecular conditions have been discussed, but the metal surface also plays an important role. As discussed in Section 1.1, different surface facets display different reaction rates, and as such the choice of the surface facet in the experiment is important as well since typically only a single facet is investigated at a time. On the other hand, with a curved crystal, both flat and stepped (or kinked) surfaces can be investigated simultaneously with varying step density[13–15]. Furthermore, the surface temperature controls whether (unwanted) reaction products desorb or not, and may influence the barrier height through surface atom motion, where the latter increases with the surface temperature[16, 17]. Additionally, the surface can be pre-covered with adsorbates[18]. This way, the surface can be (partially) passivated or a specific reaction involving multiple reactants can be investigated. In short, a large degree of control over both the molecule and the metal surface in experiments can be achieved.

From the reactive scattering of molecules from surfaces many different aspects of the mechanisms involved can be gleaned. The so-called sticking probability (i.e., the fraction of the molecules sticking to instead of scattering from the surface) is often easy to measure using the King and Wells method[19]. In the King and Wells method, the initial pressure drop in the UHV chamber when the MB first hits the surface and the initial pressure rise when the MB enters the UHV chamber without hitting the surface can be used to determine the initial sticking probability (S_0). The advantage of this method is that it is internally calibrated, and as such does not require additional calibration of the data. Other approaches to measure the sticking or reaction probability exist as well (note that sticking and reaction are not necessarily the same due to the possibility of adsorption and subsequent desorption of molecularly adsorbed molecules in the case of sticking), e.g., measuring the desorption of products during the reaction or performing temperature-programmed desorption after the reaction. However, these approaches are indirect, and require calibration of the data and assumptions about the overall reaction. Not only reacting, but also scattering molecules are often the focus of the study. For instance, the scattering angle, translational energy change, and rovibrational state-to-state scattering can be investigated to learn about the interaction between the molecule and the metal surface[9, 20–37].

However, in experiments, reaction mechanisms are mostly studied indirectly. Fortunately, theoretical studies can investigate these reaction mechanisms directly. Static calculations can investigate the potential energy surface (PES) the molecule experiences in the vicinity of the surface. Especially transition states (TSs) are of interest since they tend to be a good indicator of the reactivity. Still, instead of a single TS, molecule-metal surface reactions deal with a collection of TSs, where reaction does not necessarily occur over the TS with the lowest barrier height. Furthermore, dynamical effects arising from traveling over the PES are difficult to study with static calculations. Therefore, dynamical studies that simulate a MB hitting a surface are used to investigate both the reactivity and reaction mechanism. In such a dynamical study, many trajectory calculations are performed, with each trajectory simulating the reactive scattering for only a single initial condition. The generation of the initial conditions of the trajectories requires special care in order to mimic the experimental conditions. The benefit is that dynamical effects are included and that all relevant TSs are probed. Moreover, most, if not all, of the aforementioned experimentally obtained results can be obtained in theoretical dynamical studies as well, making comparison between experiment and theory relatively easy. Unfortunately, dynamical studies are computationally more demanding than static studies. Thus, the latter are more often performed than the former.

At present, the biggest challenge of theoretical studies is to improve their accuracy. Most theoretical studies rely on density functional theory (DFT), which requires an exchange-correlation density functional (XC-DF). In principle, an exact XC-DF exists, but its form is unknown and therefore many different approximate XC-DFs exist. Much of the ongoing research is involved with the improvement of existing XC-DFs. For example, semi-empirical DFs are developed by fitting experimental or theoretical (obtained at a higher level of theory) databases, e.g., the Minnesota DFs developed by Truhlar and coworkers[38]. In contrast, so-called non-empirical DFs are developed by ensuring that the DF fulfills several known exact limits, with the PBE DF[39] perhaps being the most famous example. In the specific reaction parameter (SRP) approach to molecule-metal surface reactions can be considered as an extreme example of a semi-empirical method: Two first-principles DFs are mixed with an empirically determined mixing parameter, yielding a chemically accurate SRP-DF for a specific molecule-metal surface reaction. Interestingly, in some cases, SRP-DFs have been found to be transferable to chemically related systems[40–42]. In this thesis, both non-empirical and SRP-DFs are employed.

Many other challenges for theoretical studies remain. The computational cost of calculations increases rapidly with the number of atoms and degrees of freedom (DOFs). Direct, or *ab initio*, molecular dynamics methods can deal with a large number of DOFs, but at a large computational cost, strongly limiting the tractability of studies employing ab initio molecular dynamics. Especially surface atom motion causes the number of DOFs to increase rapidly. Precomputed PESs can lower the computational cost considerably, but tend to struggle with a large number of DOFs, thus often neglecting surface atom motion. Fortunately, recent advances, such as the application of atomistic neural network potentials[43] and reactive force fields[44], allow for computationally relatively cheap studies with many DOFs. Furthermore, most theoretical studies neglect quantum effects in the propagation of the atoms since the cost of quantum dynamics calculations scales unfavorably with the number of DOFs. However, this neglect can be a too severe approximation, especially when light atoms such as hydrogen are involved. Another important approximation in theoretical studies is the Born-Oppenheimer approximation (BOA)[45], which separates the motion of nuclei and electrons, greatly simplifying calculations. Unfortunately, for many molecule-metal surface systems a non-negligible interaction exists between the motion of the molecule and electronic excitations in the metal surface[24, 30, 46–54], i.e., the BOA can break down due to electron-hole pair (ehp) excitation (a non-adiabatic effect). Non-adiabatic effects in molecular simulations can be treated with, for instance, mean-field (e.g., Ehrenfest dynamics[55]) or surface hopping[56] approaches. Unfortunately, those methods rely on both the ground state and the excited state(s) PESs, but the continuum of the metal surface's electrons makes the excited state PESs of molecule-metal surface systems ill-defined, limiting use of the aforementioned methods for molecule-metal surface reactions. In addition to the independent electron surface hopping model[57], which might be more accurate for molecule-metal surface systems than other surface hopping models if electron transfer to the molecule occurs or if excited electronic states of the molecule also play a role, friction models have been developed to model the dissipative effect of ehp excitation, e.g., the local density friction approximation[47] and the orbital dependent friction[49] model.

1.3 Aims of This Thesis

Many molecule-metal surface reaction mechanisms remain unclear due to their complexity. To fully understand a reaction mechanism, theoretical studies have to move beyond a static point of view (e.g., transition state theory). Therefore, in this thesis, several molecule-metal surface reaction mechanisms are studied in detail and clarified by use of molecular dynamics (MD). However, MD studies are expensive and are still limited to only a handful of molecule-metal surface reactions. To increase the range of tractable molecule-metal surface systems, not only relatively expensive *ab initio* MD studies are performed, but also the corrugation reducing procedure and the Behler-Parrinello approach to neural network potentials are employed to obtain pre-computed potential energy surfaces with which to perform MD calculations. Furthermore, at present the predictive power of theoretical studies towards experiments still wildly varies, where sometimes even the SRP approach is not sufficient in yielding a quantitative, or in some cases even a qualitatively correct, prediction. For a large part, this discrepancy between experiment and theory can be attributed to the DFT calculations, where often the DF is the culprit. Thus, the XC-DF will be given additional consideration for a few reactions in this thesis. In short, MB simulations of molecules reacting on well-defined metal surfaces are performed, with special consideration for the XC-DF and dynamical effects. The chapters in this thesis address the aforementioned aims as follows:

Chapter 2 discusses the techniques employed throughout this thesis. A brief summary of DFT is provided, with special attention to the many different available approximations to the XC-DF. We also discuss methods for precomputing PESs with a view to enabling accurate dynamics calculations of small reaction probabilities. Furthermore, some approaches in performing MD are discussed. Finally, the calculation of the observables obtained from MD calculations is described.

Chapter 3 focuses on improving the description of the HCl + Au(111) interaction through employing a state-of-the-art XC-DF and a neural network PES. The XC-DF is tested with a thorough comparison between computed and (re-analyzed) experimental results. Moreover, this chapter tries to identify the shortcomings of the XC-DF to provide guidance in future development of an accurate XC-DF for the HCl + Au(111) system.

Chapter 4 tries to elucidate the reaction mechanism behind the large effect of rotational pre-excitation of HCl on its reaction on Au(111). The state-of-the-art PES developed in Chapter 3 is employed. Especially the dynamic reorientation of the polar angle of HCl during the dissociation is investigated closely.

In **Chapter 5**, a criterium is sought that can predict when DFT at the generalized gradient approximation (GGA) level will fail at accurately describing molecule-metal surface reaction barriers. The reason for the potential failure of GGA-DFT and a potential solution to address this problem are investigated as well. Here, the focus is on the infamous O_2 + Al(111) benchmark system.

Chapter 6 tries to improve the theoretical description of the NH_3 + Ru(0001) system by including surface atom motion and Van der Waals correlation in the simulations. In some of the simulations, surface atom motion is excluded to gauge its effect on the reactivity. For the most part, the reaction mechanism is investigated since it is unexpectedly peculiar.

Chapter 7 provides predictions for the dissociation of CHD_3 on the flat surface Cu(111), the stepped surface Cu(211), and the flat single-atom alloy surfaces Pt-Cu(111) and Pd-Cu(111). The chemically accurate SRP-DF for

CHD_3 + Ni(111), Pt(111), and Pt(211) is employed in the hope to test the SRP-DF's transferability to CHD_3 + Cu surfaces with future experiments. Several dynamical effects are investigated to explain the trends observed in the reactivity of the methane-Cu surface systems.

Chapter 8 investigates the applicability of the Behler-Parrinello approach[43] to neural network potentials for reactive scattering of polyatomic molecules from mobile metal surfaces. The CHD_3 + Cu(111) system is taken as a benchmark since the associated reaction probability is too low to obtain statistically relevant data with Born-Oppenheimer MD (BOMD) for a comparison with an experimental study. Furthermore, the cause of the unusually large effect of vibrational pre-excitation of CHD_3 on the sticking probability is investigated.

Chapter 9 searches for trends in the reaction dynamics of methane on group 10 metal (111) surfaces, where BOMD is performed for the first time for CHD_3 + Pd(111). Also, the aforementioned SRP-DF for CHD_3 + Ni(111) and Pt(111) is employed. This should enable tests of the transferability of the SRP32-vdW-DF1 DF among the systems in which methane interacts with all group 10 metal (111) surfaces by experiments on CHD_3 + Pd(111) in the future.

Finally, **Chapter 10** tries to elucidate the potential reaction pathways for the dissociation of methanol and subsequent formation of formaldehyde. Moreover, the role of dynamical effects in the branching ratio of initial CH or OH dissociation is considered. The subsequent reaction step after the initial dissociation of a CH or OH bond, i.e., the formation of formaldehyde, is analyzed as well.

1.4 Main Results

Several systems have been the object of study in this thesis. Chapters 3 and 4 describe the reaction of HCl on Au(111) with a high-dimensional neural network potential (HD-NNP). This reaction is of fundamental interest since a large discrepancy between theoretical[58] and experimental[59] S_0 existed at the onset of this thesis work, despite a large effort from both a theoretical and an experimental point of view[25, 31, 58–62]. Chapter 3 shows that improvements in the DF combined with an improved analysis of experimental sticking probabilities[63] manage to largely close the gap between experiment and theory, without including non-adiatic effects. Furthermore, dynamical effects play an important role in the overall reactivity, leading to a dependence of the reactivity on impact sites that cannot be explained on the basis of site-specific barrier heights and geometries only. Interestingly, surface atom motion only has a minor influence on the sticking probability. Moreover, Chapter 4 shows that the orientation and angular momentum of HCl have a huge effect on the sticking probability on Au(111). This effect cannot be ascribed to rotational steering, but to a lock-in effect, where specific combinations of initial angular momentum and orientation allow the reaction to occur. When rotational excitation is combined with vibrational excitation an even larger effect is observed due to a mutually enforcing effect: Vibrational excitation causes the bottleneck to the dissociation to occur later along the reaction path whereas rotational excitation causes a larger distribution in the orientation to be accessible for dissociation. A very large rotational efficacy is observed, i.e., pre-exiting the molecule rotationally is much more effective at promoting reaction than increasing the collision energy or pre-exiting the molecule vibrationally.

In Chapter 5, the difference between the work function of a metal surface and the electron affinity of a molecule ($W - E_{\mathrm{ea}}$) is found to be related to a GGA DF's ability to correctly describe a molecule-metal surface reaction. If this difference is smaller, the functional also has to be made more "repulsive" in order to obtain an SRP DF. Furthermore, if $(W - E_{\mathrm{ea}}) < 7\,\mathrm{eV}$, even one of the most repulsive GGA DFs (i.e., RPBE[64]) underestimates barrier heights due to an increase in electron transfer and concomitant increase of the delocalization error fundamental to DFT[65]. Fortunately, DFs that include some (approximate) way of correcting for the so-called self-interaction error (SIE) are expected to be less susceptible to the delocalization error at the transition state, and thus potentially do not underestimate barrier heights when $(W - E_{\mathrm{ea}})$ is small. This is indeed shown to be true for the benchmark O_2 + Al(111) system. Here, the results obtained with the MS-RPBEl DF[66] suggest that meta-GGA DFs of the "made simple" (MS) kind[67] can slightly remedy the SIE problem, but not sufficiently for this system. Screened hybrid GGA DFs like HSE03-1/3X[68–70] offer an even further improved description of O_2 + Al(111) in that they yield sticking probabilities in semi-quantitative agreement with experiment[71, 72], thus offering more promise.

Dissociative chemisorption of polyatomic molecules on metal surfaces usually proceeds through either a rotationally adiabatic or a rotational sudden mechanism. The reaction is usually either direct, or proceeds through a trapped molecular physisorped state. However, Chapter 6 shows with BOMD that the reaction mechanism of NH_3 + Ru(0001) is neither rotationally adiabatic nor rotational sudden, with clearly distinct and non-statistical initial and time-of-reaction orientation distributions. Under the conditions investigated the reaction of NH_3 on Ru(0001) is not described by a simple direct, or by an indirect trapping-mediated reaction mechanism, but rather by a direct reaction mechanism in which NH_3 goes through a very short-lived molecularly chemisorbed state. Also, the lack of surface temperature dependence at high incidence energy observed by experiment[73] is confirmed with BOMD, although the modeling of surface motion is still required to accurately describe the sticking probability. Not only is surface atom motion included for this reaction for the first time, a DF incorporating attractive Van der Waals correlation[74] (RPBE-vdW-DF1) is employed as well. With respect to earlier work[75] employing the PBE DF[39] and modeling the Ru(0001) surface as static the computed sticking probability is found to be in improved agreement with experiment[73], showing reasonably good agreement between experiment and theory. This improvement is attributed to both modeling the Ru(0001) as a mobile surface and using the RPBE-vdW-DF1 DF instead of the PBE DF.

In Chapter 7, predictions are made made for the reaction of CHD_3 on Cu(111), Cu(211), and the single-atom alloys (SAAs) Pt-Cu(111) and Pd-Cu(111). The results have been obtained using static DFT and BOMD calculations with the SRP32-vdW-DF1 DF originally developed for CHD_3 + Ni(111)[76], which was later found to be chemically accurate for CHD_3 + Pt(111) and Pt(211) as well[41]. The results predict a much lower reactivity for Cu(111) than for Ni(111) and Pt(111) due to the higher and later barrier found on Cu(111), requiring higher kinetic and/or vibrational energies in order to observe reaction. Furthermore, rather surprisingly, CHD_3 has the same reaction probability on Cu(211) as on Cu(111), but with the reaction occurring only at the steps, which can be understood from the lower barriers at the step and higher barriers at the terrace relative to Cu(111). For the SAAs, the reactivity is only increased for Pt–Cu(111). In this system, reaction occurs primarily near the alloyed atom, which is not only caused by the reduction of the barrier height but also by changes in the dynamical pathway and reduction of energy transfer from methane to the surface atoms.

BOMD studies are limited to reaction probabilities larger than 1% and smaller than 99% due to the computational cost associated with the statistical accuracy requirements of reaction probabilities that fall outside of the aforementioned range. Therefore, in Chapter 8 the Behler-Parrinello approach[43] is used to develop an HD-NNP that describes a polyatomic molecule reacting on a mobile metal surface, i.e., CHD_3 + Cu(111). Here, it is shown that it is possible to use an HD-NNP for a polyatomic molecule-metal surface reaction that yields results at the accuracy level of BOMD, but with considerably reduced computational effort. While including surface atom motion explicitly, reaction probabilities as low as 5×10^{-5} have been obtained, which is intractable with BOMD at present. It is observed that the reaction probability is influenced considerably by dynamical effects such as the bobsled effect[77, 78] and surface recoil[79, 80]. A special observation for CHD_3 + Cu(111) is that a higher vibrational efficacy is obtained for two quanta in the CH stretch mode than for a single quantum, and this can be explained on the basis of the bobsled effect.

Although the SRP32-vdW-DF1 SRP-DF has been shown to be chemically accurate for CHD_3 + Ni(111) and Pt(111)[41, 76] (both group 10 metals), its transferability to Pd(111) (also a group 10 metal surface) remains unclear. Therefore, in Chapter 9, predictions have been made for the reaction of CHD_3 on Pd(111) using BOMD, while also performing a rough comparison with experimental data for CH_4 + Pd(111) obtained for lower incidence energies[81]. The reactivity of CHD_3 on Pd(111) is found to be intermediate between and similar to either Pt(111) or Ni(111), with the degree of similarity depending on the incidence energy and the initial vibrational state distribution. This is surprising because the barrier height and experiments[81] performed at lower incidence energies than investigated here suggest that the reactivity of Pd(111) should be similar to that of Pt(111) only. The relative decrease in the reactivity of Pd(111) at high incidence energies is attributed to the site specificity of the reaction and to dynamical effects such as the bobsled effect[77, 78] and energy transfer from methane to the surface atoms. In general, at the lowest incidence energy and laser-off conditions when these dynamical effects are smaller, the reaction probability on Pd(111) is comparable to that on Pt(111), which is also observed by experiment[81]. However, at higher incidence energies, these dynamical effects play a larger role and the computed reaction probability is more similar to that on Ni(111). Furthermore, under laser-on conditions ($\nu_1 = 1$) all three systems investigated show similar reaction probabilities, which is related to the aforementioned dynamical effects. The low reactivity of Pd(111) compared to that of Pt(111) is consistent with the low reactivity of Pd-Cu(111) relative to that of Pt-Cu(111) (Chapter 7), with the difference being greater than expected from the difference in barrier heights only.

An important industrial process is methanol steam reforming, which is typically used in conjunction with copper catalysts. However, little agreement exists on the reaction mechanisms involved on a copper catalyst[82]. Therefore, in Chapter 10 BOMD calculations have been performed yielding additional insight into the reaction mechanism for the dissociative chemisorption of methanol on Cu(111). Static DFT calculations on the molecule-metal surface interaction have also been performed. Here, it is shown that Cu(111) is a highly selective catalyst in that it primarily breaks the OH bond due to the difference in barrier heights and in other features of the MEPs for OH and CH cleavage. Furthermore, after the initial dissociation, formaldehyde is observed to form through three different mechanisms: Two mechanisms involve a hot hydrogen atom that either abstracts another hydrogen atom forming molecular hydrogen or knocks off another hydrogen atom resulting in two hydrogen atoms (i.e., atomically adsorbed hydrogen is formed) at the surface. In the third mechanism, the OH and CH bonds are broken simultaneously or subsequently without the influence of a hot hydrogen atom. Additionally, it is observed that at high energy, CH cleavage is the dominant pathway instead of the formerly presumed OH cleavage pathway. Finally, in order to describe the interaction of methanol with the metal surface, the SRP32-vdW-DF1 DF is used, in the hope that future experiments can validate the transferability of this SRP-DF from CH_4 + Ni(111), Pt(111), and Pt(211) to chemically related molecule-metal surface systems, like the CHD_3 + Cu(111) and Pd(111) systems investigated here.

1.5 Outlook

Here, several open questions and possible future research directions are discussed. First, the results of HCl + Au(111) (Chapters 3 and 4), O_2 + Al(111) (Chapter 5), and to a lesser extent NH_3 + Ru(0001) (Chapter 6) suggest that the XC-DF still poses a large challenge for chemically accurate predictions from DFT. Especially the delocalization error and SIE seem to play a large role in the failure of DFT to reproduce quantatively, or even qualitatively, several experiments on systems where $(W - E_{\mathrm{ea}}) > 7\,\mathrm{eV}$. Fortunately, MGGA and hybrid DFs seem to be both a pragmatic and fundamental step forward towards a correct description of such molecule-metal surface reactions. Future research could further investigate such DFs in an effort to (semi-)quantitatively reproduce experiments where charge transfer plays an important role, e.g., the aforementioned systems and systems in which O_2 interacts Cu surfaces. Additionally, non-local correlation should be included as well since it can play an important role. At present, MGGA and hybrid DFs have not yet been paired with non-local correlation in calculations on barriers for molecule-metal surface reactions. Also, the exploratory calculations in Chapter 5 suggest that non-self-consistent calculations using screened hybrid DFs might yield accurate results, but additional testing is required to validate this approach. Furthermore, it might be possible to use an HD-NNP to upscale a PES obtained at a lower level of theory (e.g., with a GGA DF) to a higher level of theory (e.g., with a hybrid DF)[83]. This way, accurate PESs can be developed while lowering the computational cost associated with accurate calculations using a high level of theory.

HCl + Au(111) remains an enigmatic system, both for theory and experiment. In order to further improve and test theory, experimental sticking probabilities with a lower error margin than presented in Chapter 3 are required. Moreover, experiments probing the rovibrational efficacies are required to validate the theoretical predictions in Chapter 4 of a huge rotational effect, in addition to a mutually enforcing effect of rotational and vibrational excitation.

A systematic experimental comparison of methane reacting on several transition metals is still lacking. For example, a large body of experimental work on methane + Ni(111) and Pt(111) exists, but a systematic comparison is difficult since the experimental conditions vary wildly. Moreover, the theoretical predictions for methane + Cu(111) and Pd(111) (Chapters 7 and 9) have yielded interesting comparisons with Ni(111) and Pt(111). However, for the Cu(111) and Pd(111) surfaces, the employed SRP32-vdW-DF1 DF is still untested against experiments using CHD_3, and therefore additional experiments are required in order to validate the SRP-DF. Likewise, the reactivity of Cu(211) and the Pt-Cu(111) and Pd-Cu(111) SAAs towards the dissociative chemisorption of methane also warrants experiments. Furthermore, although HD-NNPs allow the computation of sticking probabilities lower than 1% for methane, it is still to be seen whether the quasi-classical approach is sufficient, or whether quantum effects also need to be included for methane-metal surface systems at low incidence energies. Ring polymer MD simulations[84–86] might include quantum effects in both an efficient and an accurate manner, but requires additional testing[86].

The predictions for NH_3 + Ru(0001) in Chapter 6 warrant additional theoretical and experimental research. The accuracy of the employed XC-DF (RPBE-vdW-DF1) is questionable, in view of both the comparison to experiment and $(W - E_{\mathrm{ea}})$ being lower than 7 eV, and questions about the quality of the experimental sticking probabilities also remain. Therefore, an experiment is required to validate the previously published sticking results. Additionally, measured sticking probabilities of vibrationally pre-excited ammonia (or, preferably, NHD_2) would be a great benchmark for theory. Furthermore, an experiment where ammonia is orientationally aligned prior to hitting the metal surface, potentially using several different isotopologues of ammonia, would be able to test our prediction that the reaction is neither rotationally adiabatic nor rotational sudden, with clearly distinct and non-statistical initial and time-of-reaction orientation distributions.

The theoretical predictions for methanol + Cu(111) in Chapter 10 present several interesting conclusions, but at present no experiments are available to directly compare against. Such experiments would not only help with testing XC-DFs, but also with testing predictions of the reaction pathways, in particular concerning the formation of formaldehyde.

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