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Semi-empirical approach to the simulation of molecule-surface reaction dynamics

Migliorini, D.

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Author: Migliorini, D.

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Chapter 1

General Introduction

1.1 Heterogeneous Catalysis

Chemistry and chemical reactions play a central role in every aspect of our life: from the production of everyday materials like plastic or paper to the synthesis of medicines, from the complex metabolic cycles that sustain our body to the formation of new molecules in the interstellar medium. Chemical reactions, both in nature and in industrial processes can be facilitated and controlled using catalysts.

A catalyst is a substance that interacts with the reacting molecules and accelerates their conversion into products by providing an alternative mechanism which might be more complicated but is energetically favorable. The catalyst is then able to release the products and to return to its initial state without being modified or consumed, ready for the next catalytic cycle. In addition to increasing the conversion rate, using a catalyst may allow one to run the reaction under milder conditions and, in some cases, it can also provide selectivity, increasing the formation rate of one of the products over that of other possible and unwanted side products.

There are several different types of catalysts that can be catalogued according to their function, structure or phase. Among the most important and studied classes of catalysis we can identify three principal types of catalysis: biocatalysis, homogeneous catalysis and heterogeneous catalysis. Biocatalysis is performed by

enzymes which are proteins that act as highly specific catalysts and are involved in nearly all the metabolic processes playing a fundamental role in the biochemical reactions underlying life [1]. Homogeneous and heterogeneous catalysis, on the other hand, are defined on the basis of the phase of reactant and catalyst. The catalysis is defined as homogeneous if the reactant and the catalyst are in the same phase, which can be gaseous or more commonly liquid [2]. Finally, heterogeneous catalysis involves the presence of an interface and usually consists of a liquid or gaseous mixture reacting on a solid catalyst.

In heterogeneously catalyzed processes we often see that a transition metal based catalyst facilitates the reaction by stabilizing the molecular transition state (TS) and lowering the energy required for breaking a chemical bond [2–4], and by adsorbing the fragments that can subsequently desorb or undergo further transformation. The exploitation of heterogeneous catalysis is of extreme relevance to industry and one of the most important processes is the Haber-Bosch [3] production of ammonia (NH_3). This process takes place on an iron based catalyst [3] that promotes the cleavage of the molecular N_2 bond and subsequently the reaction with hydrogen to give ammonia:



This process has been designed by Fritz Haber, scaled up by Carl Bosch and is still today one of the main processes of ammonia production which is a fundamental building block in the synthesis of fertilizers.

Another process of great industrial relevance is steam reforming [2]. This process consists of the reforming of natural gas on a nickel based catalyst, giving as a result molecular hydrogen and carbon monoxide:



The steam reforming reaction is one of the main industrial processes used for molecular hydrogen production and it can be coupled with a second process,

called the water-gas shift reaction [4], to increase the total hydrogen yield:



A deep understanding of these catalytic processes is highly desirable and a large research effort has been made in this regard in past decades. Unfortunately, the high degree of complexity of these processes makes it extremely challenging to design and perform accurate experiments and theoretical simulations that can give insights in their overall behavior. In this Thesis we will study reactions that are important to the overall processes 1.1–1.3, in order to contribute to their understanding.

1.2 From Heterogeneous Catalysis to Surface Science (and Back)

Heterogeneously catalyzed processes, including the ones introduced in the previous Section, are usually complex multi-step processes which involve several different reactions and many molecular states. Moreover, at the industrial level, they are carried out on supported transition state metal particles which are usually poorly characterized, having different sizes and irregular shapes. Therefore, the different reaction steps can take place simultaneously and on many different sites on the catalyst. Furthermore, this kind of processes are often run at high temperature and pressure. Since most of the experimental techniques used to study surfaces rely on electrons, it is hard to perform *in situ* experiments to monitor the process under industrial conditions [5]. Moreover, it is hard to disentangle the many factors that come into play to define the mechanism and the results of these experiments. At the same time, accurate theoretical simulations of such processes in their entirety is far out of reach of present computational resources.

Microkinetic simulations [6, 7] can be used to obtain the rate of the overall process and the concentrations of reactants and products involved. In order to do

so, a set of kinetic equations needs to be defined including all the relevant reactions of the process as well as the energy of the relevant adsorption and transition states. Insights on the mechanism and on the energetics of the reactions of interest can be obtained by performing surface science experiments and theoretical simulations like the ones reported in this Thesis.

One way to tackle the study of these complicated processes is to reduce the complexity by dealing with one reaction step at the time and by using a clean single-cut metal surface to approximate the catalyst [8]. Focusing only on one (or a few) reaction steps is justified by the fact that heterogeneously catalyzed processes usually involve one or a few rate controlling steps [9] which control the overall rate of the process and therefore need to be described with high accuracy. The knowledge generated can then be used to understand the overall process and its mechanism. However, even though the contribution of surface science studies to understand heterogeneous catalysis is invaluable, several challenges need to be faced and gaps still need to be filled in order to simulate real industrial conditions.

One of the main differences between surface science and heterogeneous catalysis concerns the pressure regime under which the processes are carried out (i.e., the so called “pressure gap” [10, 11]). While in typical industrial applications the processes take place at high temperature and pressure, surface science experiments are usually performed in ultra-high vacuum (UHV). Another important aspect to consider is the so called “materials gap” [10, 11] that arises from the difference in complexity between the ideal (and often low-index) metal surface used in experiments and simulations and the real industrial catalyst. In order to improve the description of the process, all the relevant metal facets that can be found on the catalyst should be accounted for and studied. Moreover, it can happen that the catalytic activity of a particle is higher than the sum of the catalytic activities of its facets [12]. This can be due to the presence of edges between the facets that, involving undercoordinated atoms, might facilitate one of the reactions in the process [13], but also to purely kinetic reasons, like the diffusion of adsorbed species from one facet to the other [12].

One of the main goals of surface science is to contribute to the quest of design-

ing new, more efficient and cleaner catalysts. In this regard, the synergy between experiment and theoretical simulations can provide the knowledge needed to develop new and accurate microkinetic models and to improve existing ones in order to work towards the systematic design of new catalysts.

1.3 Molecules on surfaces: Possibilities and Challenges

As mentioned before, a way to improve the understanding of heterogeneously catalyzed processes is to break them down into simple reaction steps and to investigate their behavior on well defined surfaces. The improvement in the accuracy and characterization of the experiments together with the increase of computational power, allows a comparison between experimental and theoretical results that is becoming more meaningful and insightful.

Using *ab initio* molecular dynamics (AIMD) simulations and molecular beam experiments it is now possible to investigate the behavior and the reactivity of a single reaction step of a much more complex catalytical process. As discussed in Chapter 2, this helps in reducing the complexity of the problem and obtaining important insights on a rate limiting step of the process. Synergy between experiments and theory is of invaluable importance since they can be used to obtain the same observable (i.e., the zero-coverage reaction probability S_0 , studied in this Thesis) so that the comparison can give a measure of the accuracy of the theoretical model and help improve it, as discussed in Chapters 2 and 4. Moreover, performing theoretical simulations of the dissociative chemisorption of molecules on a surface can be exceptionally useful to understand the reaction mechanism, since it allows one to obtain atomic resolution of the process, which is extremely hard to achieve experimentally.

The possibility of monitoring the orientation, the internal energy and other dynamical features in “real time” during the reaction complements the information obtainable from experiments. Moreover, from the calculations it is possible

to compute important details of the underlying potential energy surface (PES) as, for example, energy barriers obtained by locating transition states (TSs) on the surface (see Figure 1.1).

Performing accurate calculations is important to being able to make meaningful comparisons with experiments. As discussed in Chapter 2, both the accuracy of the calculation and the computational cost of AIMD scale with the size of the simulation box and a compromise needs to be made. Along the same lines, it is possible to propagate the simulations only up to very few (i.e., $1 \sim 2$) picoseconds due to the high computational cost of AIMD. Moreover, in order to simulate the surface which, in principle, is infinite one needs to exploit its periodicity and represent it using a periodic metal slab. This allows one to keep the computational cost contained, but it has some drawbacks.

First of all, the unit cell has to be chosen large enough to minimize the interaction between the molecule and its first periodic replicas. Similarly, a sufficiently large vacuum space needs to be used to separate the metal slab from its periodic image. Although the computational resources available are constantly increasing, the necessity of limiting the cell size still forbids simulating the effects of isolated defects that might be important for some reactions. In addition, the limited amount of surface atoms can lead to a less accurate description of the energy dissipation.

Finally, high accuracy simulations are crucial to obtain qualitative answers from the comparison with the experiments. The work reported in this Thesis, together with the vast majority of theoretical studies in surface science, exploits density functional theory (DFT) to compute the electronic energy of the system. As extensively discussed on Chapter 2, the accuracy of DFT depends on the choice of the exchange-correlation functional (E_{XC}). The performance of a particular E_{XC} depends on the system under consideration and therefore it needs to be carefully selected. A method to systematically improve the accuracy of E_{XC} in a semi-empirical and system-specific way, by comparing the results of experiments and simulations, is at the heart of this Thesis and it will be discussed thoroughly in the following Sections and Chapters.

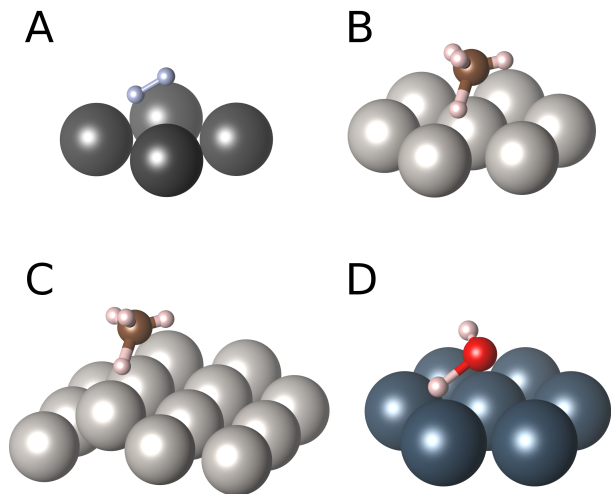


Figure 1.1: Examples of relevant transition states for the systems studied in this Thesis: (A) N_2 on $\text{W}(110)$ studied in Chapter 3, (B) CH_4 on $\text{Pt}(111)$ studied in Chapters 4, 5 and 6, (C) CH_4 on $\text{Pt}(211)$ studied in Chapters 4 and 5 and (D) H_2O on $\text{Ni}(111)$ studied in Chapter 7.

1.4 Aim of this Thesis

As discussed before, one of the main problems in the accurate simulation of the dissociative chemisorption of polyatomic molecules on a transition metal surface is the choice of the exchange correlation functional E_{XC} used to perform the DFT calculations. The main goal of this Thesis is twofold. Firstly, the static calculations and dynamical simulations reported can improve the understanding and give insights into catalytically relevant reactions. Secondly and most importantly, the main aim of this Thesis is to study how the choice of E_{XC} can influence the result of DFT calculations for molecules interacting with metal surfaces, and how developing a semi-empirical specific reaction parameter (SRP) functional [13–15] can improve the quality of said results and ultimately be used to accurately describe dissociative chemisorption reactions.

The aim of the work reported in the following Chapters of this Thesis is briefly summarized here in this Section.

Chapter 2 describes the basics of the DFT method and the semi-empirical

SRP approach that can be used to develop and test an accurate functional for a molecule-metal surface system. The Chapter reports and explains the different steps that are necessary to perform accurate AIMD simulations in order to obtain a good comparison with supersonic molecular beam experiments, which is at the heart of the semi-empirical SRP-DFT approach.

Chapter 3 reports a study aimed at testing the performance of the long-range van der Waals functional developed by Dion *et al.* (vdW-DF) [16] and its variant, called vdW-DF2, developed by Lee *et al.* [17]. It has been shown [13, 15, 18] that using a functional that models vdW interactions can improve the accuracy of DFT calculations for catalytically relevant systems. In the study reported in this Chapter, the vdW-DF and the vdW-DF2 functionals are tested for N₂ on W(110), a prototypical surface science system for which quantitative agreement between theory and experiments has not yet been achieved [19–22].

Chapter 4 focuses on the transferability of an SRP functional among chemically related systems. The SRP functional originally developed to describe the dissociative chemisorption of CHD₃ on Ni(111) [15] (called SRP32-vdW functional) is tested here on the dissociation of the same molecule on Pt(111) [13]. Most importantly, the work reported in Chapter 4 also studies the transferability among systems in which CHD₃ interacts with different facets of the same transition metal in order to go from the flat Pt(111) to more catalytically relevant and “defected” surfaces such as the stepped Pt(211) surface. The aim of this work is to provide a simple and systematic strategy to predict chemically accurate barriers for different surface sites of catalytically relevant systems.

Chapter 5 reports a study where the chemically accurate SRP32-vdW functional is used to obtain dynamically relevant features of the dissociative chemisorption of CHD₃ on the flat Pt(111) and on the stepped Pt(211) surfaces [23]. The aim of this work is to understand how the under-coordinated step site of the Pt(211) surface influences the reactivity and how the different topology of the surface can alter the dissociation dynamics.

Chapter 6 compares the performance of a standard GGA functional (i.e., PBE [24]) with that of the SRP32-vdW functional for CHD₃ on Pt(111) [13, 15]. The

aim of this Chapter is to investigate why the SRP32-vdW functional reproduces experiments whereas the PBE functional does not, even though the two functionals return a very similar geometry and energy for the minimum barrier [25].

Chapter 7 takes the first step in the development of an SRP functional for a different system for which chemical accuracy has not yet been achieved: HOD on Ni(111) [26]. Here the SRP functional developed for methane is used as an initial guess to obtain a prediction for plausible molecular beam experiments for this system. Another aim of this Chapter is to obtain useful dynamical insights on this relevant process while treating all the DOFs, including surface motion, in the simulation. Moreover, another important purpose of this work is to show that molecular beam experiments for HOD on Ni(111) can be accurately simulated (i.e., with reaction probabilities $> 1\%$ for incidence energies achievable with molecular beams) in the hope to motivate other scientists to provide well-characterized experiments on this system. This would make it possible to eventually derive an accurate density functional for the investigated process.

1.5 Main Results

The main results of the work reported in the following Chapters of this Thesis are summarized in this Section.

Chapter 3 | Application of van der Waals Functionals to the Calculation of Dissociative Adsorption of N_2 on W(110) for Static and Dynamic Systems

In Chapter 3 we report a study of the static potential energy surface (PES) and of the reaction probability of N_2 on W(110). The study has been performed on a DFT level using functionals that include the correlation part developed by Dion *et al.* [16] (called vdW-DF) and its revised version (vdW-DF2) [17]. We find that using the vdW-DF2 functional improves the description of the molecule-surface interaction compared to GGA functionals like PBE and RPBE, by giving generally shallower molecular adsorption wells and barriers for the indirect reaction

and for the molecular desorption more similar to each other, as suggested by experiments [27]. The vdW-DF2 functional is then used to perform AIMD simulations of molecular beam experiments [28, 29] for which the agreement between experiment and theory is, at best, qualitative [19–22]. Despite the improvements in the description of the static PES, the reactivity computed through AIMD simulations does not depend much on the incidence energy (E_i), similarly to what was observed with PBE and RPBE [22], because of the competition between the direct and the indirect reaction mechanisms. The dependence of reaction on incident energy found experimentally [28, 29] is therefore not reproduced. The AIMD results show that the less deep molecular adsorption wells lead to a reduced indirect reaction probability, especially for normal incidence. However, the barrier for the direct dissociation computed with the vdW-DF2 functional might still be too large.

Chapter 4 | Surface Reaction Barriometry: Methane Dissociation on Flat and Stepped Transition Metal Surfaces

In Chapter 4 we study the transferability of the SRP32-vdW functional, which was initially developed to reproduce experiments for CHD_3 on $\text{Ni}(111)$ with chemical accuracy [15]. In this Chapter we show that the same functional can be used to model the same reaction on a different low-index transition metal surface (i.e., $\text{Pt}(111)$) with chemical accuracy [13]. Furthermore, the SRP32-vdW functional is also transferable to methane interacting with the “defected” $\text{Pt}(211)$ surface, which has under-coordinated step sites. The transferability of the SRP functional among systems in which a specific molecule interacts with different facets of the same metal allows us to define a semi-empirical protocol, which we call “reaction barriometry”, that can help bridge the materials gap between surface science and heterogeneous catalysis. The strategy can be summarized as follows: (I) accurate molecular beam experiments are performed for a molecule dissociating over an ideal low index surface. (II) an SRP functional is developed for said system by comparing AIMD and experimental results. (III) the SRP functional is tested on a different experiment for the same system. (IV) the transferabil-

ity demonstrated in this Chapter can then be exploited to obtain chemically accurate barriers (i.e., with errors smaller than 4.2 kJ/mol) on all the relevant surface cuts of the metal studied, including stepped surfaces and, presumably, edges and corners of nanoparticles. The results can be used as a benchmark for future theoretical work, new methodological approximations and (hopefully) to perform accurate microkinetic simulations of catalytic processes proceeding over nanoparticles of the metal studied.

Chapter 5 | Methane on a Stepped Surface: Dynamical Insights on the Dissociation of CHD_3 on Pt(111) and Pt(211)

In Chapter 5 we report an extensive analysis of 12500 AIMD trajectories run performed using the SRP32-vdW functional on the flat Pt(111) and the stepped Pt(211) surface. The results show that, even though the difference in minimum barrier height results in a significantly different reactivity [23], the reaction mechanism is very similar on the two surfaces. This can be explained by the similar geometry of the TSs on the two surfaces and by the known absence of rotational steering [13, 15, 23, 30], which requires the molecules to be preoriented in a geometry similar to that of the TS in order to react. It has also been shown that the molecular trapping observed on the Pt(211) surface but not on the Pt(111) surface can partially be explained by the larger energy transfer to surface phonons on the stepped surface. In addition the geometry of the stepped surface promotes energy transfer to parallel motion, resulting in trapped molecules which retain a relatively large velocity parallel to the surface. Together with the long estimated trapping time (i.e., ≈ 43 ps), this suggests that experimentally the trapped molecules have time to explore a large portion of the surface and possibly to react by finding the most favorable geometry or even a higher order defect, like a kink.

Chapter 6 | CHD₃ Dissociation on Pt(111): a Comparison of the Reaction Dynamics Based on the PBE Functional and on a Specific Reaction Parameter Functional

In Chapter 6 we compare the performance of two density functionals on the description of the reaction of CHD₃ on Pt(111). The functionals under consideration are the well-known PBE [24] functional and the SRP32-vdW functional developed for CHD₃ on Ni(111) [15]. The TS associated with the minimum barrier has been computed with the two functionals. The calculations show a very similar barrier geometry and the same barrier height within 0.6 kJ/mol. However, while the SRP32-vdW functional reproduces molecular beam experiments with chemical accuracy [13], the PBE functional considerably overestimates the reaction probability [25]. We found that the van der Waals well described by the correlation part [16] of the SRP32-vdW functional, and not present with the PBE functional, accelerates the trajectories towards the surface, leaving the molecule less time to distort towards the TS geometry and leading to a larger energy transfer to the surface phonons. These factors play a role in lowering the reactivity computed using the SRP32-vdW functional with respect to that obtained using the PBE functional and therefore contribute to the improved agreement with the experimental results.

Chapter 7 | HOD on Ni(111): Ab Initio Molecular Dynamics Prediction of Molecular Beam Experiments

In Chapter 7 we report a predictive AIMD study for molecular beam experiments on the dissociative chemisorption of HOD on Ni(111) for which, at present, no experimental results are available. Our study improves the description of the system over previous theoretical work [31] by explicitly treating all the degrees of freedom of the surface through AIMD simulations and by using the SRP functional developed for CHD₃ (SRP32-vdW) [15] that models long-range vdW interactions [16, 32], which are important for this type of system [13, 15, 18]. The analysis of the trajectories confirmed the strong mode [33, 34] and bond [35]

selectivity of the reaction and suggested rotational steering plays an important role. Molecules have been observed to react regardless of their initial orientation, while the bonds were steered towards their orientation in the TS at the time of the dissociation. Most importantly, comparing our results with experiments performed on a similar system (D_2O on $\text{Ni}(111)$ [36]), we find that the SRP32-vdW functional is a good starting point for developing an SRP functional for HOD on $\text{Ni}(111)$. The comparison seems to suggest that the SRP32-vdW would overestimate the reactivity for the system studied. Therefore, when experimental results become available, the mixing parameter of the functional (which currently has a low value) can be increased to make the functional describe a more repulsive interaction so that the AIMD simulations reproduce the experimental results.

1.6 Outlook

In this Section the questions that remain open from the work presented in this Thesis are reported and discussed, together with an outlook on the possible directions in which this research could be developed in the future.

At present, the understanding of the dissociative chemisorption of N_2 on $\text{W}(110)$ is still poor. In order to develop an SRP functional for the system, one would need a weighted average of two density functionals that, coupled with AIMD, are able to reproduce the shape of the experimental reactivity curve (i.e., its dependence on the collision energy, see Chapter 2). Once these two functionals have been identified, the procedure illustrated in Chapter 2 can be exploited to devise and test a semi-empirical functional that might be able to accurately reproduce molecular beam experiments, hence giving important dynamical insights on this reaction. Currently, neither standard GGA functionals such as PBE and RPBE [22] or a functional including van der Waals interactions like the vdW-DF2 [37] has been successful. In order to be able to accurately reproduce experiments for this system, one needs a functional able to properly describe both the dissociative chemisorption and the molecular adsorption and desorption processes observed. A problem with this is that the GGA functionals that de-

scribe molecular adsorption and dissociative adsorption well tend to differ. For instance, the RPBE functional does rather well at describing molecular adsorption [38], but tends to overestimate dissociative chemisorption barriers [14, 39]. A possible solution to this problem might be the development of a meta-GGA [40] based SRP functional. Further work would be needed to improve the understanding of N_2 on $\text{W}(110)$, both on the theoretical side, as mentioned above, and on the experimental side. To the best of our knowledge there are only two molecular beam experiment results available for the system [28, 29] and they report rather different results, complicating the comparison with theoretical simulations. The availability of new and well characterized molecular beam experiments would help in the quest for a candidate SRP functional by allowing theoreticians to design better and more comparable AIMD simulations.

The transferability of the SRP functional discussed in Chapter 4 opens new possibilities to improve the accuracy of existing microkinetic simulations which rely on computed barrier heights to obtain reaction rates. The SRP functional can be exploited to compute chemically accurate barriers on different surface sites and defects that can be found in real catalytic conditions, therefore improving the quality of the description.

Further investigation is also required to fully understand the difference in reactivity observed for CHD_3 on $\text{Pt}(111)$ using the PBE and the SRP32-vdW functionals, as described in Chapter 6. Using the modified Baule model [41] to estimate the dependence of the energy transfer (E_T) to the surface on the molecular collision energy and on the depth of the molecular adsorption well, suggests that only roughly half of the energy shift between the reaction probability curves can be explained with the larger E_T observed for the SRP32-vdW functional and due to the van der Waals interactions modeled by its correlation part. Further work might shed light on the dynamical effects behind what is left to explain of the difference in reactivity between the two functionals.

The work reported in Chapter 7 on HOD on $\text{Ni}(111)$ represents the initial step to developing an accurate density functional for said system. In order to further proceed towards this goal, well characterized molecular beam experiments

are needed for conditions at which AIMD is applicable. As soon as experimental results become available, the SRP32-vdW functional used in our study [13, 15, 26] can be tuned to try to reproduce the experimental results with chemical accuracy. This could help improve the understanding of this catalytically relevant system.

Along the same line, having developed an SRP functional for CHD_3 on Pt and Ni surfaces, the next natural step in the line of work presented in this Thesis would be to tackle the dissociative chemisorption of CHD_3 on Pd(111) to test if the SRP32-vdW functional is transferable to yet another group X transition metal. Moreover, the transferability of said functional to other surface cuts could be tested on Pt surfaces with kinks, like the Pt(210) surface, to be used as a model system for nanoparticle corners. In the Theoretical Chemistry group of Leiden, work along these lines is already underway.

The SRP approach could also be extended to other different and, possibly, more complex reactions involved in catalytic processes. Besides the study discussed in Chapter 7 on HOD on Ni(111), other relevant processes of choice would be, for example, the dissociation of methanol (CH_3OH) or ammonia (NH_3) on a metal surface.

Having an SRP functional also allows one to obtain information on dynamically relevant features of a process, as shown in Chapters 5 and 7, but, unfortunately, at this stage AIMD can not accurately predict reactivities below 1% (see Chapter 2 for more details). This limitation can be circumvented by coupling high-dimensional PESs developed using a Neural Network method [42, 43], which also model surface motion [44–47], with chemically accurate SRP functionals. This will allow one to run a large number of computationally cheap quasi-classical trajectories and hence to obtain statistically significant results for low reaction probabilities.

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