Development of highly accurate density functionals for H2 dissociation on transition metals

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1 General Introduction

1.1 Gas-surface reactions

In heterogeneous catalysis new products are formed through elementary reactions of molecules with surfaces. The chemistry of small molecules reacting on a surface are therefore an integral part of our everyday lives. Examples include the production of plastic and other everyday materials, the production of ammonia which enables the use of artificial fertilizer[1], the polution reduction achieved by the use of a catalytic converter in a car[2], or the steam reforming proces which is currently used to produce hydrogen (H_2) and carbon monoxide (CO) gas from methane (CH_4) and steam[3]. Gas-surface reactions are also not solely the preserve of human activity. A rusting bit of iron left outside in a humid environment is also an example of a gas-surface reaction: oxygen gas (O_2) from the air has reacted with the metal surface of the iron forming rust. Chemical reactions that proceed using a catalyst are extremely important to the chemical industry. Improvements in the design of catalysts, either by allowing cheaper materials to be used as catalysts or reducing the energy cost of a given reaction, have a potentially huge impact on the chemical industry[4].

In its simplest form a chemical reaction entails two reactants coming together with enough energy to overcome the energetic barrier to reaction and then reacting to form the product(s). A catalyst is a reaction partner that interacts with the reactants in order to provide an alternative reaction mechanism that can be more complicated but is energetically 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 to reaction and fascilitating the breaking of existing chemical bonds and the formation of new chemical bonds. After the reaction the resulting products move away from the catalyst, allowing the catalyst to go into a new catalytic cylce. Lowering the energetic barrier to a reaction by using a catalyst can thus not only increase the reaction rate but also allow the reaction to proceed under milder conditions (lower temperature and or pressure), reducing the cost. In some cases it is even possible to increase the selectivity of particular reaction such that the

formation of a desired reaction product is favored over an unwanted reaction product, reducing waste and polution.

In heterogeneous catalysis the reactants and the catalyst exist in different phases (plasma, gas, liquid, solid), 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 for nearly all biochemical reactions underpinning life as we know it[5].

Usually a heterogeneously catalysed process does not consist of a single reaction step. A reaction that takes place on a catalytic surface can be described as a complex proces consisting of several elementary reaction steps. An example that includes some possible elementary reaction steps is a molecule that adsorbs on a surface and diffuses to a reaction site before dissociating. It thus goes through the elementary steps of adsorption, diffusion and dissociation at a reactive site. In 2007 Ertl was awarded the Nobel prize in chemistry for investigating elementary reaction steps in heterogeneous catalysis experimentally[6].

The elementary reaction steps in heterogeneous catalysis form a complex network of reactions. The most important steps in such a network are called the rate-limiting steps. Creating a theoretical description of a complex reaction network ideally starts with the calculation of 'chemically accurate' barrier heights for elementary reaction steps[7]. Note that the calculation of chemically accurate reaction rates of reaction networks is also important to the search for extraterrestrial life in the solar system[8] and in the field of astrochemistry[9–11]. In heterogeneous catalysis the rate-limiting step is often the dissociative chemisorption of a molecule on a surface[12,13]. Calculating chemically accurate barrier heights for rate-controlling reactions to obtain accurate rates of the overall reaction network[14] is a rather complex task that not only needs to take into account the static electronic structures of both reactant and the catalytic surface at the transition state, but 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[15].

1.2   H$_2$ reacting on metal surfaces

Metal surfaces from a group of effective catalysts for the reaction of small molecules such as H$_2$. The electrons of a metal are delocalized while the electrons of molecules are more localized around their constituent atoms[16]. The grouping of the metal electrons in bands, some of which are close to the Fermi level, allows the metal surface to readily donate to or accept an electron from

the molecule at hardly any energetic cost[17–19]. This possibility of electron exchange is what makes metal surfaces particularly effective catalysists.

The research presented in this thesis focussus on the reaction of H_2 on metal surfaces. The dissociation of H_2 is relevant to the industrial synthesis of methanol from CO_2 over a $Cu/ZnO/Al_2O_3$ catalyst, since in this process the dissociation of H_2 is considered to be the rate-limiting step[20–22]. H_2 dissociation on transition metal surfaces is an important process in hydrogenation catalysis[23]. Hydrogenation of unsaturated bonds in organic molecules through heterogeneous catalysis on solids has extensive uses in the chemical industry[24–29]. Although the basic elementary reaction steps of H_2 dissociation and hydrogenation reactions have been elucidated long ago by Horiuti and Polanyi[30], many open questions and research opportunities remain with respect to efficiency, selectivity, and catalytic particle or surface design and geometry[23].

The kinetics of H_2 dissociation, recombinative desorption, and scattering has predominantly been studied under ultra high vacuum (UHV) conditions[31–71]. However, very little is known about the dynamics of H_2 dissociation at industrially relevant temperatures and pressures[72,73] (often denoted as the temperature and pressure gaps).

Scattering of H_2 from reactive metal surfaces is also of interest for fundamental reasons, for the wealth of phenomena that have been investigated and uncovered by experiments on this topic. Reaction probability versus collision energy curves can be obtained from molecular beam experiments[32,33,38,48,51–53,60–64,74] and associative desorption experiments[32,34,38,50,75]. Associative desorption experiments also yield information on the effect of the initial rovibrational state[32,34,38,50,75] and the alignment of the molecule relative to the surface normal on the reverse dissociative chemisorption reaction[36]. Molecular beam experiments in which H_2 scatters from a surface can provide final state resolved information on vibrational excitation[40], rotationally elastic[31] and inelastic[41] scattering, and vibrationally and rotationally inelastic scattering[42,66] Elastic and inelastic diffractive scattering of H_2 from metal surfaces can be adressed as well[67–71,76–80].

In order to improve the predictive power of theory with respect to the catalytic activity of small molecules reacting at metal surfaces, the way in which metal surfaces modify the potential energy of molecules needs to be understood at a fundamental level. The elementary reaction steps of a molecule interacting with a surface can be investigated experimentally using techniques that exert control over the various degrees of freedom of a molecule reacting on a cold metal surface. The work presented in this thesis is predominantly concerned with the description and simulation of supersonic molecular beam experiments[32,33,38,48,51–53,60–64,74] and associative desorption

experiments[34,38,50,54,55,75,81–83]. In the molecular beam technique, pioneerd by King and Wells[84], a gas supersonically expands into a UHV chamber towards the target after being collimated by the use of skimmers. Initially the gas entering the target chamber will be blocked in some way until a steady state gas pressure is reached in the target chamber. Once the blockade between the collimated stream of supersonic gas (the molecular beam) and the target is removed the molecular beam will hit the target surface. Some molecules will react with the target causing the pressure in the target chamber to drop. The initial drop in pressure is directly proportional to the sticking probability of molecules in the molecular beam to the target surface in the zero coverage limit[84]. Various degrees of freedom of the molecules in the molecular beam can be controlled by adjusting the temperature of the nozzle through which the gas expands into to the UHV chamber, by adjusting the backpressure of the gas, or by changing the gas mixture. The importance of the molecular beam technique to catalysis research cannot be understated[85–88].

Another approach to experimentally assess the potential energy landscape of a molecule interacting with a surface is conducting associative desorption experiments[34,38,50,54,55,75,81–83], in which often state-specific information can be obtained by using the resonance-enhanced multi-photon ionization (REMPI) technique[32,34,38,50,75]. This bottom up approach allows for the disentanglement of the many competing effects present under real catalytic conditions, such as high temperatures and pressures.

1.3   Aims and scope of this thesis

The main goal of the thesis is to improve the theoretical description of reactive scattering of H_2 from various transition metal surfaces, such as Cu(111), Cu(211), Ag(111), Au(111) and Pt(111). The starting point for any theoretical description of the interaction of H_2 with a metal surface presented in this thesis will be the time-dependent Schrödinger equation[89]. Specifically the aim will be to close the gap between theory and experiment with respect to the description of the reactivity ánd state-specific reaction dynamics, through the design of highly accurate density functionals.

In Chapter 2 the theory behind the dynamical methods used to simulate molecular beam experiments is discussed. First the solving of the electronic structure problem using DFT will be discussed, as well as how potential energy surfaces (PESs) can be constructed for relaxed ideal zero kelvin surfaces using the corrugation reducing procedure[90]. The two dynamics methods used in this thesis, namely the quasi-classical trajectory (QCT) method and the quantum dynamics (QD) method, will be introduced. The last section of Chapter 2

will deal with the calculation of observables that is needed to compare to experimental observations.

In Chapter 3 the aim is to determine whether, with a meta generalized gradient approximation (meta-GGA) functional constructed within the "made simple" approach, it is possible to get a chemically accurate description of the dissociative chemisorption of H_2 on Cu(111), while at the same time obtaining a better description of the Cu lattice than possible with previous SRP functionals based on the generalized gradient approximation (GGA). A second goal is to determine whether with the meta-GGA "made simple" functionals constructed here it should be possible to also get a more accurate description of the dissociative chemisorption of H_2 on and its associative desorption from Ag(111) than was previously possible with the SRP48 GGA functional for H_2 + Cu(111).

In Chapter 4 the focus lies on the stepped nature of the Cu(211) unit cell and whether the dynamics of H_2 impinging on Cu(211) can still be described by quasi-classical techniques. To this end a large number of time-dependent wave packet calculations are carried out for all rovibrational states populated in a molecular beam experiment according to the nozzle temperature.

In Chapter 5 new specific reaction parameter (SRP) density functionals at the GGA level that include non-local correlation are introduced for the H_2 + Cu(111) system. Application of these newly designed functionals to the H_2 + Ag(111), Au(111) and Pt(111) systems might allow for the identification of critical components of a density functional that make it transferable among systems in which the same molecule interacts with different metal surfaces.

In Chapter 6 the mGGA density functionals developed in Chapter 3 are combined with rVV10[91] non-local correlation. The effectiveness of the newly constructed density functionals is evaluated for the H_2 + Cu(111), Ag(111), Au(111) and Pt(111) systems. Additionally the transferability of the newly constucted density functionals is assessed using the methodology first introduced in Chapter 5.

1.4   Main results

The main results obtained during the research that resulted in this thesis are summarized in this section.

Chapter 3: Specific reaction parameter density functional based on the meta-generalized gradient approximation: Application to H_2 + Cu(111) and H_2 + Ag(111)

Three density functionals at the meta-GGA level have been constructed based on the "made simple" approach[92,93], namely the MS-PBEl, MS-B86bl and MS-RPBEl density functionals. Here the 'l' stands for 'like', in that the gradient enhancement factors of the functionals are based on PBE-like[94], B86b-like[95], or RPBE-like[96] expressions but with $\mu = \frac{10}{81}$ as is appropriate for metallic bonding[97,98]. In the made simple approach to constructing a meta-GGA density functional, a function of the kinetic energy density is defined that effectively allows one to vary the exchange functional according to whether the binding in a certain region is metallic or covalent. The three new MS meta-GGA functionals yield lattice constants that are in excellent agreement with zero-point energy corrected experimental values. Likewise, the interlayer lattice spacing relaxations for the top two layers of Cu(111) and Ag(111) are in good agreement with experiment. The performance of the three new MS meta-GGA functionals was found to be comparable to PBEsol[97], a density functional specifically designed for the solid state. The barrier heights and geometries obtained for H_2 + Cu(111) were in good agreement with those obtained earlier with the original SRP functional for H_2 + Cu(111)[99]. More importantly, the sticking probability curves computed with the three MS functionals and the QCT method agreed with experiments of Rettner and Auerbach and co-workers and of Rendulic and co-workers to within chemical accuracy. Furthermore, the sticking probability curves computed with the MS-PBEl and MS-B86bl functionals for D_2 + Ag(111) agree slightly better with the molecular beam experiments of Hodgson and co-workers than dynamics calculations based on the SRP48 GGA functional designed for H_2 + Cu(111). Good agreement is also obtained between initial-state selected reaction probabilities computed for H_2 and D_2 + Ag(111) and the initial-state selected reaction probabilities extracted from associative desorption experiments of Hodgson and co-workers on these systems. Based on the obtained results it can be concluded that, (i) it is possible to construct non-empirical meta-GGA "made simple" functionals for these two H_2-metal systems that describe the dissociative chemisorption reaction as accurately as previous semiempirical functionals based on GGA functionals, while simultaneously giving a more accurate description of the metal lattice, and (ii) on the basis of these MS functionals (in particular, MS-PBEl and MS-RPBEl), an SRP-DF can be constructed for H_2 + Cu(111), but not for H_2 + Ag(111).

Chapter 4: Quantum dynamics of dissociative chemisorption of H_2 on the stepped Cu(211) surface

A full quantum dynamical molecular beam simulation has been performed for the reaction of H_2 on Cu(211). To the this end a large number of time-dependent wave packet (TDWP) calculations have been performed to obtain fully initial-state resolved reaction probabilities for all rovibrational states that are relevant to the simulation of molecular beam sticking experiments. The main conclusion is that the reaction of H_2 with Cu(211) is well described quasi-classically. This is especially true when simulating molecular beam experiments where one averages over a large number of rovibrational states and a wide velocity distribution. It has however been found that some small differences between QD and QCT calculations remain, most notably with respect to the extent to which the reaction depends on the alignment of H_2. The QD method predicts stronger alignment effects on the reactivity than the QCT method for low lying rotational states. A comparison to recent associative desorption experiments suggests and direct dynamics calculation that incorporate surface atom motion appear to show that the effect of surface atom motion and ehp's on the reactivity falls within chemical accuracy, even for the high surface temperature used in the associative desorption experiments. In contrast to the theoretical and experimental results for D_2 reacting on Cu(111) and Cu(100), at low translational energy a sharp downturn of the rotational quadrupole alignment parameters is observed for vibrationally excited molecules. This downturn can be attributed to a site specific reaction mechanism of inelastic rotational enhancement. The results show that the stepped Cu(211) surface is distinct from its component Cu(111) terraces and Cu(100) steps and cannot be described as a combination of its component parts with respect to the reaction dynamics when considering the orientational dependence.

Chapter 5: Designing new SRP density functionals including non-local vdW-DF2 correlation for H_2 + Cu(111) and their transferability to H_2 + Ag(111), Au(111) and Pt(111)

New specific reaction parameter (SRP) density functionals that include non-local vdW-DF2[100] correlation have been constructed for the H_2 (D_2) + Cu(111) system, namely the B86SRP68-DF2 and SRPsol63-DF2 density functionals. The transferability of these density functionals to the H_2 (D_2) + Ag(111), H_2 (D_2) + Au(111) and H_2 (D_2) + Pt(111) systems has been investigated. All newly tested and developed density functionals are based on GGA-exchange and use non-local correlation to describe dissociative chemisorption of H_2 (D_2) on Cu(111) within chemical accuracy, and, to the extent that it can be assessed,

improve the transferability to the other systems discussed in this Chapter over the previously reported SRP48 and MS-B86bl SRP density functionals. Two SRP density functionals that include non-local correlation, namely B86SRP68-DF2 and PBEα57-DF2[101], are transferable from the highly activated late barrier H_2 + Cu(111) system to the weakly activated early barrier H_2 + Pt(111) system and vice versa. This feat could not be demonstrated with GGA and meta-GGA SRP density functionals that do not include non-local correlation. Assessing the transferability of the tested and developed SRP density functionals to H_2 + Ag(111) and H_2 + Au(111) is difficult due to the lack of well characterized molecular beam experiments for Ag(111) and their complete absence for Au(111). A detailed analysis of associative desorption experiments on Cu(111) suggests that accurate calculation of $E_{1/2}(\nu, J)$ parameters requires an improvement of our dynamical model. Describing the surface degrees of freedom might close the gap between the excellent description of dissociative chemisorption and the good description of associative desorption, for molecules in the vibrational ground state. Any discrepancy in predicted reactivity between simulated associative desorption and dissociative chemisorption remaining after taking into account the effect of surface atom motion can then most likely be attributed to electron-hole pair excitation. Lack of additional experiments for the H_2 + Au(111) system, specifically a well described dissociative chemisorption experiment, presently keeps us from disentangling the effects of surface reconstruction, surface temperature and ehp excitation for this system. Additionally a full molecular beam simulation using QD is presented for the H_2 + Cu(111) system using the B86SRP68-DF2 density functional, which is the best performing density functional for H_2 + Cu(111), and which also gives a good description of the Van der Waals interaction in this system. Overall the H_2 + Cu(111) system is very well described quasi-classically when looking at molecular beam sticking probabilities or degeneracy averaged initial-state selected reaction probabilities.

Chapter 6: Performance of made-simple meta-GGA functionals with rVV10 non-local correlation for H_2 + Cu(111), D_2 + Ag(111), H_2 + Au(111) and D_2 + Pt(111)

The three made simple mGGA density functionals designed in Chapter 3 have been combined with rVV10[91] in order to obtain the MS-PBEl-rVV10, MS-B86bl-rVV10 and MS-RPBEl-rVV10 density functionals. All three developed density functionals can describe the molecular beam dissociative chemisorption experiment of D_2 reacting on Ag(111) with chemical accuracy, and that the MS-B86bl-rVV10 density functional can describe two sets of molecular beam dissociative chemisorption experiments of D_2 reacting on Pt(111) with chemical

accuracy. Additionally, by calculating $E_{1/2}(\nu, J)$ parameters for the H$_2$ (D$_2$) + Au(111) system and comparing to experimental $E_0(\nu, J)$ parameters chemical accuracy is obtained with the MS-PBEl-rVV10 density functional. Assessing the performance of the three developed MS mGGA DFs for the H$_2$ (D$_2$) + Au(111) system is difficult due the absence of well characterized molecular beam experiments and of calculations using a reconstructed Au(111) surface that incorporate surface motion, as also discussed in Chapter 5. Of the three developed density functionals MS-PBEl-rVV10 performs excellently with respect to the known Van der Waals well geometries. The MS-B86bl-rVV10 and MS-RPBEl-rVV10 density functionals yield Van der Waals well geometries that are somewhat too shallow. In a comparisson to initial-state resolved experiments on H$_2$ (D$_2$) + Ag(111) an excellent agreement with experiment is observed in the case of H$_2$, for all three developed density functionals. With respect to the molecular beam sticking probabilities of H$_2$ (D$_2$) + Cu(111) the three developed density functionals yield sticking probabilities in line with sticking probabilities predicted by the PBE[94] density functional, which are too high. The three original made simple mGGA density functionals gave a description of the metal that was comparable to the PBEsol[97] density functional. We find that combining them with rVV10[91] non-local correlation comes at the cost of a slightly less good description of the metal. In general lattice constants become somewhat smaller than zero-point energy corrected experimental results. However, the slight underestimation of the calculated lattice constants is still smaller than the overestimation of calculated lattice constants generally found with the best current SRP density functionals that include vdW-DF2[100] non-local correlation. The three developed density functionals also predict that the interlayer distance of the top two layers of the six layer slabs that have been used tend to expand somewhat, in contrast to experimental observations. The obtained results show that climbing Jakob's ladder[102] yields increasingly more accurate results for most systems for the gas-surface systems of H$_2$ (D$_2$) interacting with transition metals.

1.5   Outlook

The development of (SRP) density functionals that can describe the reaction of H$_2$ with multiple transition metal surfaces to within chemical accuracy is a good step forward in the theoretical description of such systems, however many open questions still remain. These questions are however difficult to answer without either additional experimental observations or improvements to the dynamical model, the implementation of which will lead to increased computational cost of the calculations. This section will highlight further research opportunities

that can potentially improve the theoretical description of H_2 interacting with transition metal surfaces.

Further development in theoretical descriptions of small molecules reacting with transition metal surfaces can be roughly segmented in three areas. One of these areas would be the improvement of the dynamical model, by taking into account thermal surface atom motion. Another of these research directions would be climbing Jacob's ladder[102] towards screened hybrid functionals. The third area can be described by approaches that attempt to go beyond the Born-Oppenheimer approximation[103], thus beyond purely electronically adiabatic dynamics calculations.

The dynamics calculations presented in this thesis assume an ideal relaxed 0 K surface, thus surface atom motion according to the surface temperature is neglected. Adiabatic dynamics calculations on a ground state electronic PES and using the static surface approximation have been shown to work well for the activated reaction of H_2 on cold transition metals[15,104–108]. Associative desorption experiments are however carried out on very hot surfaces[34,38,50]. In these experiments surface atom motion cannot be readily ignored.

Currently surface atom motion can be taken into account by performing direct dynamics calculations in which the forces are calculated on the fly using DFT[107,109–112]. This is however computationally very expensive, which makes it difficult to obtain accurate statistics. Another approach is to obtain a high dimensional PES that can accomodate surface atom motion using the Behler-Parrinello approach to construct a generalized neural network representation of a high dimensional PES[113]. The neural network approach allows for comparatively cheap quasi-classical dynamics calculations once the neural network has been trained to a large batch of electronic structure calculations for random geometries of H_2 above thermally distorted transition metal slabs. This method has now been succesfully applied to create high dimensional neural network potentials for the reaction of small molecules with transition metals[114–117]. Applying this method to the reaction of H_2 with transition metals would make it possible to test the assumption that molecular beam dissociative chemisorption experiments and associative desorption experiments are linked through detailed belance. As discussed in Chapter 5, when incorporating surface atom motion, the remaining difference between predictions made by theory and experiment can then be safely attributed to non-adiabatic effects such as electron-hole pair excitations. Additionally, if such a high dimensional neural network PES would be available, this would allow direct simulation of associative desorption experiments by running trajectories starting around the transition state using Metropolis sampling of the initial conditions[118–122]. Although this has to some extent already been done, earlier work[119,120] used a PES that is an

approximate fit[123] to unconverged DFT calculations[124] using the PW91 density functional[125], and the statistical accuracy of the results of the later work[122] was limited by the number of trajectories that could be run due to the direct dynamics method employed. Performing such calculations with the highly accurate density functionals presented in this thesis might answer some of the open questions raised by earlier work[118–122].

Note that high dimensional neural network potentials may be difficult to implement in QD calculations[126]. The static corrugation model (SCM)[106,127] in combination with the sudden approximation can potentially be used in QD calculations, where multiple QD calculations could be performed for differently initialized surface displacements.

A second way to improve the theoretical description of H_2 interacting with transition metal surfaces may be to climb Jacob's ladder[102]. The density functionals developed in the research that resulted in this thesis are based on the GGA or meta-GGA, a logical next step would be to move towards (screened) hybrid density functionals[128] combined with non-local correlation[129]. As the transferability of meta-GGA based density functionals that include non-local correlation developed in Chapter 6 has demonstrated, climbing to a higher rung on Jacob's ladder has the potential to yield more generally applicable density functionals. Some advances have been made using this approach with the notoriously difficult O_2 + Al(111) system[130–132] and other systems[133]. However, it is unclear whether hybrid density functionals will be better for H_2 - late transition metal surface systems. For these systems, $(\Phi - EA)$ tends to exceed 7 eV, where Φ is the workfunction of the metal and EA the electron affinity of the molecule. For such systems semi-local exchange appears to work quite well[132]. Also, calculations with (screened) hybrid density functionals are computationally very demanding. It will therefore be difficult to go beyond the static surface approximation when using hybrid density functionals in the forseeable future.

The third area in which the theoretical description of H_2 interacting with transition metal surfaces can be improved is by going beyond the Born-Oppenheimer approximation[103]. The lack of a band gap for electronic excitations in a metal allows for energy exchange of the molecule with the surface through electron-hole pair excitations. The effect of electron-hole pair excitations can be modelled as a classical friction force in molecular dynamics with electronic friction (MDEF) calculations[134]. In Chapter 4 this is done in the simplest possible way, by using the local density friction approximation (LDFA) together with the independent atom approximation (IAA)[135,136]. In this approach molecular properties are neglected, as the off-diagonal elements of the friction tensor expressed in Cartesian coordinates of the atoms are taken to

be zero. Therefore kinetic coupling between different degrees of freedom cannot be described in this model. To move beyond this limitation orbital-dependent friction (ODF) could be used in future dynamics calculations[137–139]. However the effects of incorporating ODF in the reaction dynamics of H_2 are small and require additional experiments for theoretical predictions to be verified[139] and for proving that ODF should be better.

As suggested in Chapters 5 and 6 there is a need for more, more varied, and more accurately described experiments. Presently DFT is the only electronic structure method that is simultaneously computationally cheap and accurate enough to map out full PESs and make large comparative studies feasible. Within the SRP approach to DFT currently[140] experimental observations are neccesary as a benchmark for density functional design. When looking at the H_2 + Ag(111) and H_2 + Au(111) systems considered in this thesis, one stark realization is that further development of chemically accurate density functionals for H_2 reacting on transition metal surfaces is still heavily stymied by a lack of experimental data. This is bad news as presently semi-empirical DFT seems to be the only path forward to extracting chemically accurate information on barriers to reaction. Relying on non-empirical constraints in density functional design is not guaranteed to yield better overall accuracy, as illustrated by the poor performance of the SCAN[141] density functional for H_2 + Cu(111)[142]. For both the activated and non-activated reactions of H_2 on transitions metals there is now only a single well studied system, namely H_2 + Cu(111) (and maybe H_2 + Pt(111)[143]) (see Chapter 5).

Finally, and this is best illustrated by the work on H_2 (D_2) reacting on Ag(111) in Chapter 5, many density functionals predict roughly similar molecular beam sticking probabilities but different initial-state resolved reaction probabilities. Observations from new and more detailed experiments could lead the way, and show which theoretical model is more in line with reality. Initial-state resolved reaction probabilities, rotational quadrupole alignment parameters, vibrational efficacies, and inelastic scattering probabilties are more sensitive to the details of the PES[144]. However, accurately described measurements of these observables are sparse[36,41,50,54,55].

References

(1) Ertl, G. Primary steps in catalytic synthesis of ammonia. *J. Vac. Sci. Technol.* **1983**, *1*, 1247–1253.

(2) Bagot, P. A. J. Fundamental surface science studies of automobile exhaust catalysis. *J. Mater. Sci. Technol.* **2004**, *20*, 679–694.

(3) Chorkendorff, I.; Niemantsverdriet, J. W., *Concepts of modern catalysis and kinetics*; John Wiley & Sons, Weinheim: 2017.

(4) Park, G. B.; Kitsopoulos, T. N.; Borodin, D.; Golibrzuch, K.; Neuge-bohren, J.; Auerbach, D. J.; Campbell, C. T.; Wodtke, A. M. The kinetics of elementary thermal reactions in heterogeneous catalysis. *Nature Rev. Chem.* **2019**, *3*, 723–732.

(5) Voet, D.; Voet, J. G., *Biochemistry, 4th Edition*; NewYork: John Wiley & SonsInc: 2011; Vol. 492.

(6) Ertl, G. Reactions at surfaces: from atoms to complexity (Nobel lecture). *Angew. Chem. Int. Ed.* **2008**, *47*, 3524–3535.

(7) Kroes, G.-J. Toward a database of chemically accurate barrier heights for reactions of molecules with metal surfaces. *J. Phys. Chem lett.* **2015**, *6*, 4106–4114.

(8) Sousa-Silva, C.; Seager, S.; Ranjan, S.; Petkowski, J. J.; Zhan, Z.; Hu, R.; Bains, W. Phosphine as a biosignature gas in exoplanet atmospheres. *Astrobiology* **2020**, *20*, 235–268.

(9) Viti, S.; Holdship, J. In *Machine Learning in Chemistry: The Impact of Artificial Intelligence*; The Royal Society of Chemistry, Cambridge: 2020, pp 195–205.

(10) Jørgensen, J. K.; Belloche, A.; Garrod, R. T. Astrochemistry during the formation of stars. *Annu. Rev. Astron. Astrophys.* **2020**, *58*, 727–778.

(11) Yao, Y.; Giapis, K. P. Dynamic molecular oxygen production in cometary comae. *Nat. Comm.* **2017**, *8*, 1–8.

(12) Wolcott, C. A.; Medford, A. J.; Studt, F.; Campbell, C. T. Degree of rate control approach to computational catalyst screening. *J. Catal.* **2015**, *330*, 197–207.

(13) Sabbe, M. K.; Reyniers, M.-F.; Reuter, K. First-principles kinetic modeling in heterogeneous catalysis: an industrial perspective on best-practice, gaps and needs. *Catal. Sci. Technol.* **2012**, *2*, 2010–2024.

(14)   Stegelmann, C.; Andreasen, A.; Campbell, C. T. Degree of rate control: how much the energies of intermediates and transition states control rates. *J. Am. Chem. Soc.* **2009**, *131*, 8077–8082.

(15)   Kroes, G.-J.; Díaz, C. Quantum and classical dynamics of reactive scattering of H_2 from metal surfaces. *Chem. Soc. Rev.* **2016**, *45*, 3658–3700.

(16)   Hoffmann, R. Building bridges between inorganic and organic chemistry (Nobel Lecture). *Angew. Chem. Int. Ed.* **1982**, *21*, 711–724.

(17)   Kiselev, V. F.; Krylov, O. V., *Adsorption and catalysis on transition metals and their oxides*; Springer Science & Business Media, New York: 2012; Vol. 9.

(18)   Hammer, B.; Nørskov, J. Electronic factors determining the reactivity of metal surfaces. *Surf. Sci.* **1995**, *343*, 211–220.

(19)   Hammer, B.; Nørskov, J. Why gold is the noblest of all the metals. *Nature* **1995**, *376*, 238.

(20)   Waugh, K. Methanol synthesis. *Catal. Today* **1992**, *15*, 51–75.

(21)   Grabow, L.; Mavrikakis, M. Mechanism of methanol synthesis on Cu through CO_2 and CO hydrogenation. *Acs Catalysis* **2011**, *1*, 365–384.

(22)   Behrens, M.; Studt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L., et al. The active site of methanol synthesis over $Cu/ZnO/Al_2O_3$ industrial catalysts. *Science* **2012**, *336*, 893–897.

(23)   Zaera, F. The surface chemistry of metal-based hydrogenation catalysis. *ACS Catal.* **2017**, *7*, 4947–4967.

(24)   Rylander, P. N., *Hydrogenation methods*; Academic Press: London: 1990.

(25)   Veldsink, J. W.; Bouma, M. J.; Schöön, N. H.; Beenackers, A. A. Heterogeneous hydrogenation of vegetable oils: a literature review. *Cata. Rev.: Sci. Eng.* **1997**, *39*, 253–318.

(26)   Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective hydrogenation for fine chemicals: Recent trends and new developments. *Adv. Synth. Catal.* **2003**, *345*, 103–151.

(27)   Chen, B.; Dingerdissen, U.; Krauter, J. G. E.; Rotgerink, H. G. J. L.; Möbus, K.; Ostgard, D. J.; Panster, P.; Riermeier, T.; Seebald, S.; Tacke, T., et al. New developments in hydrogenation catalysis particularly in synthesis of fine and intermediate chemicals. *Appl. Catal. A* **2005**, *280*, 17–46.

(28) Mäki-Arvela, P.; Hájek, J.; Salmi, T.; Murzin, D. Y. Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts. *Appl. Catal. A* **2005**, *292*, 1–49.

(29) Hu, C.; Creaser, D.; Siahrostami, S.; Grönbeck, H.; Ojagh, H.; Skoglundh, M. Catalytic hydrogenation of C $=\!=$ C and C $=\!=$ O in unsaturated fatty acid methyl esters. *Catal. Sci. Technol.* **2014**, *4*, 2427–2444.

(30) Horiuti, I.; Polanyi, M. Exchange reactions of hydrogen on metallic catalysts. *Trans. Faraday Soc.* **1934**, *30*, 1164–1172.

(31) Gostein, M.; Parhikhteh, H.; Sitz, G. Survival probability of H_2 ($\nu = 1$, J$= 1$) scattered from Cu(110). *Phys. Rev. Lett.* **1995**, *75*, 342.

(32) Michelsen, H.; Rettner, C.; Auerbach, D.; Zare, R. Effect of rotation on the translational and vibrational energy dependence of the dissociative adsorption of D_2 on Cu(111). *J. Chem. Phys.* **1993**, *98*, 8294–8307.

(33) Berger, H.; Leisch, M.; Winkler, A.; Rendulic, K. A search for vibrational contributions to the activated adsorption of H_2 on copper. *Chem. Phys. Lett.* **1990**, *175*, 425–428.

(34) Kaufmann, S.; Shuai, Q.; Auerbach, D. J.; Schwarzer, D.; Wodtke, A. M. Associative desorption of hydrogen isotopologues from copper surfaces: characterization of two reaction mechanisms. *J. Chem. Phys.* **2018**, *148*, 194703.

(35) Anger, G.; Winkler, A.; Rendulic, K. Adsorption and desorption kinetics in the systems H_2/Cu(111), H_2/Cu(110) and H_2/Cu(100). *Surf. Sci.* **1989**, *220*, 1–17.

(36) Hou, H.; Gulding, S.; Rettner, C.; Wodtke, A.; Auerbach, D. The stereodynamics of a gas-surface reaction. *Science* **1997**, *277*, 80–82.

(37) Comsa, G.; David, R. The purely "fast" distribution of H_2 and D_2 molecules desorbing from Cu(100) and Cu(111) surfaces. *Surf. Sci.* **1982**, *117*, 77–84.

(38) Rettner, C.; Michelsen, H.; Auerbach, D. Quantum-state-specific dynamics of the dissociative adsorption and associative desorption of H_2 at a Cu(111) surface. *J. Chem. Phys.* **1995**, *102*, 4625–4641.

(39) Rettner, C.; Auerbach, D.; Michelsen, H. Dynamical studies of the interaction of D_2 with a Cu(111) surface. *J. Vac. Sci. Technol. A* **1992**, *10*, 2282–2286.

(40) Rettner, C.; Michelsen, H.; Auerbach, D. Determination of quantum-state-specific gas—surface energy transfer and adsorption probabilities as a function of kinetic energy. *Chem. Phys.* **1993**, *175*, 157–169.

(41)   Hodgson, A.; Samson, P.; Wight, A.; Cottrell, C. Rotational excitation
       and vibrational relaxation of H$_2$ ($\nu=$ 1, J= 0) Scattered from Cu(111).
       Phys. Rev. Lett. **1997**, *78*, 963–966.

(42)   Watts, E.; Sitz, G. O. State-to-state scattering in a reactive system: H$_2$
       (v= 1, j= 1) from Cu(100). *J. Chem. Phys.* **2001**, *114*, 4171–4179.

(43)   Michelsen, H.; Rettner, C.; Auerbach, D. On the influence of surface
       temperature on adsorption and desorption in the D$_2$/Cu(111) system.
       Surf. Sci. **1992**, *272*, 65–72.

(44)   Okazawa, T.; Takeuchi, F.; Kido, Y. Enhanced and correlated thermal
       vibrations of Cu(111) and Ni(111) surfaces. *Physical Review B* **2005**,
       72, 075408.

(45)   Lindgren, S.; Walldén, L.; Rundgren, J.; Westrin, P. Low-energy electron
       diffraction from Cu(111): subthreshold effect and energy-dependent
       inner potential; surface relaxation and metric distances between spectra.
       Phys. Rev. B **1984**, *29*, 576–588.

(46)   Chae, K.; Lu, H.; Gustafsson, T. Medium-energy ion-scattering study
       of the temperature dependence of the structure of Cu(111). *Phys. Rev.
       B* **1996**, *54*, 14082.

(47)   Andersson, S.; Persson, M. Sticking in the physisorption well: influence
       of surface structure. *Phys. Rev. Lett.* **1993**, *70*, 202.

(48)   Cao, K.; Füchsel, G.; Kleyn, A. W.; Juurlink, L. B. Hydrogen adsorption
       and desorption from Cu(111) and Cu(211). *Phys. Chem. Chem. Phys.*
       2018, *20*, 22477–22488.

(49)   Harten, U.; Toennies, J. P.; Wöll, C. Molecular beam translational spec-
       troscopy of physisorption bound states of molecules on metal surfaces.
       I. HD on Cu(111) and Au(111) single crystal surfaces. *J. Chem. Phys.*
       1986, *85*, 2249–2258.

(50)   Shuai, Q.; Kaufmann, S.; Auerbach, D. J.; Schwarzer, D.; Wodtke, A. M.
       Evidence for electron–hole pair excitation in the associative desorption
       of H$_2$ and D$_2$ from Au(111). *J. Phys. Chem. Lett.* **2017**, *8*, 1657–1663.

(51)   Luntz, A.; Brown, J.; Williams, M. Molecular beam studies of H$_2$ and
       D$_2$ dissociative chemisorption on Pt(111). *J. Chem. Phys.* **1990**, *93*,
       5240–5246.

(52)   Groot, I.; Ueta, H.; Van der Niet, M.; Kleyn, A.; Juurlink, L. Supersonic
       molecular beam studies of dissociative adsorption of H$_2$ on Ru(0001). *J.
       Chem. Phys.* **2007**, *127*, 244701.

(53) Cottrell, C.; Carter, R.; Nesbitt, A.; Samson, P.; Hodgson, A. Vibrational state dependence of D_2 dissociation on Ag(111). *J. Chem. Phys.* **1997**, *106*, 4714–4722.

(54) Murphy, M.; Hodgson, A. Translational energy release in the recombinative desorption of H_2 from Ag(111). *Surf. Sci.* **1997**, *390*, 29–34.

(55) Murphy, M.; Hodgson, A. Role of surface thermal motion in the dissociative chemisorption and recombinative desorption of D_2 on Ag(111). *Phys. Rev. Lett.* **1997**, *78*, 4458–4461.

(56) Resch, C.; Berger, H.; Rendulic, K.; Bertel, E. Adsorption dynamics for the system hydrogen/palladium and its relation to the surface electronic structure. *Surf. Sci.* **1994**, *316*, L1105–L1109.

(57) Beutl, M.; Riedler, M.; Rendulic, K. D. Strong rotational effects in the adsorption dynamics of H_2/Pd(111): evidence for dynamical steering. *Chem. Phys. Lett.* **1995**, *247*, 249–252.

(58) Beutl, M.; Lesnik, J.; Rendulic, K.; Hirschl, R.; Eichler, A.; Kresse, G.; Hafner, J. There is a true precursor for hydrogen adsorption after all: the system H2/Pd (1 1 1)+ subsurface V. *Chem. Phys. Lett.* **2001**, *342*, 473–478.

(59) Gostein, M.; Sitz, G. O. Rotational state-resolved sticking coefficients for H_2 on Pd(111): testing dynamical steering in dissociative adsorption. *J. Chem. Phys.* **1997**, *106*, 7378–7390.

(60) Steinrück, H.-P.; Rendulic, K.; Winkler, A. The sticking coefficient of H_2 on Ni(111) as a function of particle energy and angle of incidence: A test of detailed balancing. *Surf. Sci.* **1985**, *154*, 99–108.

(61) Robota, H. J.; Vielhaber, W.; Lin, M.-C.; Segner, J.; Ertl, G. Dynamics of interaction of H_2 and D_2 with Ni(110) and Ni(111) surfaces. *Surf. Sci.* **1985**, *155*, 101–120.

(62) Hayward, D.; Taylor, A. The variation of the sticking probability of hydrogen and deuterium on Ni(111) with energy and angle of incidence. *Chem. Phys. Lett.* **1986**, *124*, 264–267.

(63) Resch, C.; Zhukov, V.; Lugstein, A.; Berger, H.; Winkler, A.; Rendulic, K. Dynamics of hydrogen adsorption on promoter-and inhibitor-modified nickel surfaces. *Chem. Phys.* **1993**, *177*, 421–431.

(64) Salmeron, M.; Gale, R. J.; Somorjai, G. A. Molecular beam study of the H_2–D_2 exchange reaction on stepped platinum crystal surfaces: Dependence on reactant angle of incidence. *J. Chem. Phys.* **1977**, *67*, 5324–5334.

(65) Gee, A. T.; Hayden, B. E.; Mormiche, C.; Nunney, T. S. The role of steps in the dynamics of hydrogen dissociation on Pt(533). *J. Chem. Phys.* **2000**, *112*, 7660–7668.

(66) Gostein, M.; Watts, E.; Sitz, G. O. Vibrational relaxation of H_2 ($\nu = 1$, J = 1) on Pd(111). *Phys. Rev. Lett.* **1997**, *79*, 2891–2894.

(67) Goncharova, L. V.; Braun, J.; Ermakov, A. V.; Bishop, G. G.; Smilgies, D.-M.; Hinch, B. J. Cu(001) to HD energy transfer and translational to rotational energy conversion on surface scattering. *J. Chem. Phys.* **2001**, *115*, 7713–7724.

(68) Nieto, P.; Farías, D.; Miranda, R.; Luppi, M.; Baerends, E. J.; Somers, M. F.; van der Niet, M. J. T. C.; Olsen, R. A.; Kroes, G.-J. Diffractive and reactive scattering of H_2 from Ru(0001): experimental and theoretical study. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8583–8597.

(69) Whaley, K. B.; Yu, C.-f.; Hogg, C. S.; Light, J. C.; Sibener, S. J. Investigation of the spatially anisotropic component of the laterally averaged molecular hydrogen/Ag(111) physisorption potential. *J. Chem. Phys.* **1985**, *83*, 4235–4255.

(70) Berndt, R.; Toennies, J. P.; Wöll, C. Evidence for coupled rotational and phonon quantum excitation in the scattering of a nearly monoenergetic HD beam from the Ni(001) surface. *J. Chem. Phys.* **1990**, *92*, 1468–1477.

(71) Laurent, G.; Barredo, D.; Farías, D.; Miranda, R.; Díaz, C.; Riviere, P.; Somers, M. F.; Martín, F. Experimental and theoretical study of rotationally inelastic diffraction of D_2 from NiAl(110). *Phys. Chem. Chem. Phys.* **2010**, *12*, 14501–14507.

(72) Johansson, M.; Skulason, E.; Nielsen, G.; Murphy, S.; Nielsen, R. M.; Chorkendorff, I. Hydrogen adsorption on palladium and palladium hydride at 1 bar. *Surf. Sci.* **2010**, *604*, 718–729.

(73) Fiordaliso, E. M.; Murphy, S.; Nielsen, R.; Dahl, S.; Chorkendorff, I. H_2 splitting on Pt, Ru and Rh nanoparticles supported on sputtered HOPG. *Surf. Sci.* **2012**, *606*, 263–272.

(74) Rendulic, K.; Anger, G.; Winkler, A. Wide range nozzle beam adsorption data for the systems H_2/nickel and H_2/Pd(100). *Surf. Sci.* **1989**, *208*, 404–424.

(75) Sementa, L.; Wijzenbroek, M.; Van Kolck, B.; Somers, M.; Al-Halabi, A.; Busnengo, H. F.; Olsen, R.; Kroes, G.-J.; Rutkowski, M.; Thewes, C., et al. Reactive scattering of H_2 from Cu(100): comparison of dynamics calculations based on the specific reaction parameter approach to density functional theory with experiment. *J. Chem. Phys.* **2013**, *138*, 044708.

(76) Cowin, J. P.; Yu, C.-F.; Sibener, S. J.; Wharton, L. HD scattering from Pt(111): rotational excitation probabilities. *J. Chem. Phys.* **1983**, *79*, 3537–3549.

(77) Yu, C.-f.; Whaley, K. B.; Hogg, C. S.; Sibener, S. J. Investigation of the spatially isotropic component of the laterally averaged molecular hydrogen/Ag(111) physisorption potential. *J. Chem. Phys.* **1985**, *83*, 4217–4234.

(78) Nieto, P.; Pijper, E.; Barredo, D.; Laurent, G.; Olsen, R. A.; Baerends, E.-J.; Kroes, G.-J.; Farías, D. Reactive and nonreactive scattering of H_2 from a metal surface is electronically adiabatic. *Science* **2006**, *312*, 86–89.

(79) Bertino, M. F.; Hofmann, F.; Toennies, J. P. The effect of dissociative chemisorption on the diffraction of D_2 from Ni(110). *J. Chem. Phys.* **1997**, *106*, 4327–4338.

(80) Farías, D.; Díaz, C.; Rivière, P.; Busnengo, H.; Nieto, P.; Somers, M.; Kroes, G.; Salin, A.; Martín, F. In-plane and out-of-plane diffraction of H_2 from metal surfaces. *Phys. Rev. Lett.* **2004**, *93*, 246104.

(81) Michelsen, H. A.; Auerbach, D. J. A critical examination of data on the dissociative adsorption and associative desorption of hydrogen at copper surfaces. *J. Chem. Phys.* **1991**, *94*, 7502–7520.

(82) Wetzig, D.; Dopheide, R.; Rutkowski, M.; David, R.; Zacharias, H. Rotational Alignment in Associative Desorption of D_2 ($\nu'' = 0$ and 1) from Pd(100). *Phys. Rev. Lett.* **1996**, *76*, 463–466.

(83) Darling, G. R.; Holloway, S. Vibrational effects in the associative desorption of H_2. *Surf. Sci.* **1992**, *268*, L305–L310.

(84) King, D. A.; Wells, M. G. Molecular beam investigation of adsorption kinetics on bulk metal targets: Nitrogen on tungsten. *Surf. Sci.* **1972**, *29*, 454–482.

(85) Smith Jr, J. N. Molecular beam scattering from solid surfaces: A critical review. *Surf. Sci.* **1973**, *34*, 613–637.

(86) D'Evelyn, M. P.; Madix, R. J. Reactive scattering from solid surfaces. *Surf. Sci. Rep.* **1983**, *3*, 413–495.

(87)   Libuda, J.; Freund, H.-J. Molecular beam experiments on model cata-
        lysts. *Surf. Sci. Rep.* **2005**, *57*, 157–298.

(88)   Zaera, F. Use of molecular beams for kinetic measurements of chemical
        reactions on solid surfaces. *Surf. Sci. Rep.* **2017**, *72*, 59–104.

(89)   Schrödinger, E. An undulatory theory of the mechanics of atoms and
        molecules. *Phys. Rev.* **1926**, *28*, 1049–1070.

(90)   Busnengo, H.; Salin, A.; Dong, W. Representation of the 6D potential
        energy surface for a diatomic molecule near a solid surface. *J. Chem.
        Phys.* **2000**, *112*, 7641–7651.

(91)   Sabatini, R.; Gorni, T.; De Gironcoli, S. Nonlocal van der Waals density
        functional made simple and efficient. *Phys. Rev. B* **2013**, *87*, 041108.

(92)   Sun, J.; Xiao, B.; Ruzsinszky, A. Communication: Effect of the orbital-
        overlap dependence in the meta generalized gradient approximation. *J.
        Chem. Phys.* **2012**, *137*, 051101.

(93)   Sun, J.; Haunschild, R.; Xiao, B.; Bulik, I. W.; Scuseria, G. E.; Perdew,
        J. P. Semilocal and hybrid meta-generalized gradient approximations
        based on the understanding of the kinetic-energy-density dependence.
        J. Chem. Phys. **2013**, *138*, 044113.

(94)   Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approxi-
        mation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(95)   Becke, A. D. On the large-gradient behavior of the density functional
        exchange energy. *J. Chem. Phys.* **1986**, *85*, 7184–7187.

(96)   Hammer, B. H. L. B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption
        energetics within density-functional theory using revised Perdew-Burke-
        Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.

(97)   Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria,
        G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the density-
        gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.*
        2008, *100*, 136406.

(98)   Hamada, I. van der Waals density functional made accurate. *Phys. Rev.
        B* **2014**, *89*, 121103.

(99)   Díaz, C.; Pijper, E.; Olsen, R.; Busnengo, H.; Auerbach, D.; Kroes, G.
        Chemically accurate simulation of a prototypical surface reaction: H_2
        dissociation on Cu(111). *Science* **2009**, *326*, 832–834.

(100) Lee, K.; Murray, É. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-accuracy van der Waals density functional. *Phys. Rev. B* **2010**, *82*, 081101.

(101) Ghassemi, E. N.; Wijzenbroek, M.; Somers, M. F.; Kroes, G.-J. Chemically accurate simulation of dissociative chemisorption of D_2 on Pt(111). *Chem. Phys. Lett.* **2017**, *683*, 329–335.

(102) Perdew, J. P.; Schmidt, K. In *AIP Conf. Proc.* 2001; Vol. 577, pp 1–20.

(103) Born, M.; Oppenheimer, R. Zur quantentheorie der molekeln. *Ann. Phys.* **1927**, *389*, 457–484.

(104) Díaz, C.; Olsen, R. A.; Auerbach, D. J.; Kroes, G.-J. Six-dimensional dynamics study of reactive and non reactive scattering of H_2 from Cu(111) using a chemically accurate potential energy surface. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6499–519.

(105) Wijzenbroek, M.; Somers, M. F. Static surface temperature effects on the dissociation of H_2 and D_2 on Cu(111). *J. Chem. Phys.* **2012**, *137*, 054703.

(106) Spiering, P.; Wijzenbroek, M.; Somers, M. An improved static corrugation model. *J. Chem. Phys.* **2018**, *149*, 234702.

(107) Nattino, F.; Genova, A.; Guijt, M.; Muzas, A. S.; Díaz, C.; Auerbach, D. J.; Kroes, G.-J. Dissociation and recombination of D_2 on Cu(111): Ab initio molecular dynamics calculations and improved analysis of desorption experiments. *J. Chem. Phys.* **2014**, *141*, 124705.

(108) Nieto, P.; Pijper, E.; Barredo, D.; Laurent, G.; Olsen, R. A.; Baerends, E.-J.; Kroes, G.-J.; Farías, D. Reactive and nonreactive scattering of H_2 from a metal surface is electronically adiabatic. *Science* **2006**, *312*, 86–89.

(109) Füchsel, G.; Cao, K.; Er, S.; Smeets, E. W. F.; Kleyn, A. W.; Juurlink, L. B. F.; Kroes, G.-J. Anomalous dependence of the reactivity on the presence of steps: dissociation of D_2 on Cu(211). *J. Phys. Chem. Lett.* **2018**, *9*, 170–175.

(110) Nattino, F.; Migliorini, D.; Kroes, G.-J.; Dombrowski, E.; High, E. A.; Killelea, D. R.; Utz, A. L. Chemically accurate simulation of a polyatomic molecule-metal surface reaction. *J. Phys. Chem. Lett.* **2016**, *7*, 2402–2406.

(111)   Migliorini, D.; Chadwick, H.; Nattino, F.; Gutiérrez-González, A.; Dombrowski, E.; High, E. A.; Guo, H.; Utz, A. L.; Jackson, B.; Beck, R. D., et al. Surface reaction barriometry: methane dissociation on flat and stepped transition-metal surfaces. *J. Phys. Chem. Lett.* **2017**, *8*, 4177–4182.

(112)   Gerrits, N.; Chadwick, H.; Kroes, G.-J. Dynamical study of the dissociative chemisorption of CHD_3 on Pd(111). *J. Phys. Chem. C* **2019**, *123*, 24013–24023.

(113)   Behler, J.; Parrinello, M. Generalized neural-network representation of high-dimensional potential-energy surfaces. *Phys. Rev. Lett.* **2007**, *98*, 146401.

(114)   Gerrits, N.; Shakouri, K.; Behler, J.; Kroes, G.-J. Accurate probabilities for highly activated reaction of polyatomic molecules on surfaces using a high-dimensional neural network potential: CHD_3 + Cu(111). *J. Phys. Chem. Lett.* **2019**, *10*, 1763–1768.

(115)   Shakouri, K.; Behler, J.; Meyer, J.; Kroes, G.-J. Accurate neural network description of surface phonons in reactive gas-surface dynamics: N_2+ Ru(0001). *J. Phys. Chem. Lett.* **2017**, *8*, 2131–2136.

(116)   Gerrits, N.; Geweke, J.; Smeets, E. W. F.; Voss, J.; Wodtke, A. M.; Kroes, G.-J. Closing the Gap Between Experiment and Theory: Reactive Scattering of HCl from Au(111). *J. Phys. Chem. C* **2020**, *124*, 15944–15960.

(117)   Zhu, L.; Zhang, Y.; Zhang, L.; Zhou, X.; Jiang, B. Unified and transferable description of dynamics of H_2 dissociative adsorption on multiple copper surfaces via machine learning. *Phys. Chem. Chem. Phys.* **2020**, *22*, 13958–13964.

(118)   Perrier, A.; Bonnet, L.; Liotard, D.; Rayez, J.-C. On the dynamics of H_2 desorbing from a Pt(111) surface. *Surf. Sci.* **2005**, *581*, 189–198.

(119)   Perrier, A.; Bonnet, L.; Rayez, J.-C. Dynamical study of H_2 and D_2 desorbing from a Cu(111) surface. *J. Phys. Chem. A* **2006**, *110*, 1608–1617.

(120)   Perrier, A.; Bonnet, L.; Rayez, J.-C. Statisticodynamical approach of final state distributions in associative desorptions. *J. Chem. Phys.* **2006**, *124*, 194701.

(121)   Díaz, C.; Perrier, A.; Kroes, G. Associative desorption of N_2 from Ru(0001): a computational study. *Chem. Phys. Lett.* **2007**, *434*, 231–236.

(122) Galparsoro, O.; Kaufmann, S.; Auerbach, D. J.; Kandratsenka, A.; Wodtke, A. M. First principles rates for surface chemistry employing exact transition state theory: application to recombinative desorption of hydrogen from Cu(111). *Phys. Chem. Chem. Phys.* **2020**, *22*, 17532–17539.

(123) Dai, J.; Zhang, J. Z. Quantum adsorption dynamics of a diatomic molecule on surface: four-dimensional fixed-site model for H_2 on Cu(111). *J. Chem. Phys.* **1995**, *102*, 6280–6289.

(124) Hammer, B.; Scheffler, M.; Jacobsen, K. W.; Nørskov, J. K. Multidimensional potential energy surface for H_2 dissociation over Cu(111). *Phys. Rev. Lett.* **1994**, *73*, 1400–1403.

(125) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46*, 6671–6687.

(126) Manzhos, S.; Dawes, R.; Carrington, T. Neural network-based approaches for building high dimensional and quantum dynamics-friendly potential energy surfaces. *Int. J. Quant. Chem.* **2015**, *115*, 1012–1020.

(127) Wijzenbroek, M.; Somers, M. Static surface temperature effects on the dissociation of H_2 and D_2 on Cu(111). *J. Chem. Phys.* **2012**, *137*, 054703.

(128) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.

(129) Berland, K.; Jiao, Y.; Lee, J.-H.; Rangel, T.; Neaton, J. B.; Hyldgaard, P. Assessment of two hybrid van der Waals density functionals for covalent and non-covalent binding of molecules. *J. Chem. Phys* **2017**, *146*, 234106.

(130) Livshits, E.; Baer, R.; Kosloff, R. Deleterious effects of long-range self-repulsion on the density functional description of O_2 sticking on aluminum. *J. Phys. Chem. A* **2009**, *113*, 7521–7527.

(131) Liu, H.-R.; Xiang, H.; Gong, X. First principles study of adsorption of O_2 on Al surface with hybrid functionals. *J. Chem. Phys.* **2011**, *135*, 214702.

(132) Gerrits, N.; Smeets, E. W. F.; Vuckovic, S.; Powell, A. D.; Doblhoff-Dier, K.; Kroes, G.-J. Density functional theory for molecule–metal surface reactions: When does the generalized gradient approximation get it right, and what to do if it does not. *J. Phys. Chem. Lett,* **2020**, *11,* 10552–10560.

(133) Mallikarjun Sharada, S.; Bligaard, T.; Luntz, A. C.; Kroes, G.-J.; Nørskov, J. K. Sbh10: A benchmark database of barrier heights on transition metal surfaces. *J. Phys. Chem. C* **2017**, *121,* 19807–19815.

(134) Alducin, M.; Muiño, R. D.; Juaristi, J. Non-adiabatic effects in elementary reaction processes at metal surfaces. *Prog. Surf. Sci.* **2017**, *92,* 317–340.

(135) Juaristi, J.; Alducin, M.; Muiño, R. D.; Busnengo, H. F.; Salin, A. Role of electron-hole pair excitations in the dissociative adsorption of diatomic molecules on metal surfaces. *Phys. Rev. Lett.* **2008**, *100,* 116102.

(136) Puska, M. J.; Nieminen, R. M. Atoms embedded in an electron gas: Phase shifts and cross sections. *Phys. Rev. B* **1983**, *27,* 6121–6128.

(137) Askerka, M.; Maurer, R. J.; Batista, V. S.; Tully, J. C. Role of tensorial electronic friction in energy transfer at metal surfaces. *Phys. Rev. Lett.* **2016**, *116,* 217601.

(138) Maurer, R. J.; Jiang, B.; Guo, H.; Tully, J. C. Mode specific electronic friction in dissociative chemisorption on metal surfaces: H 2 on Ag (111). *Physical review letters* **2017**, *118,* 256001.

(139) Spiering, P.; Meyer, J. Testing electronic friction models: vibrational de-excitation in scattering of H_2 and D_2 from Cu(111). *J. Phys. Chem. Lett.* **2018**, *9,* 1803–1808.

(140) Doblhoff-Dier, K.; Meyer, J.; Hoggan, P. E.; Kroes, G.-J. Quantum Monte Carlo calculations on a benchmark molecule-metal surface reaction: H_2 + Cu(111). *J. Chem. Theory Comput.* **2017**, *13,* 3208–3219.

(141) Sun, J.; Ruzsinszky, A.; Perdew, J. P. Strongly constrained and appropriately normed semilocal density functional. *Phys. Rev. Lett.* **2015**, *115,* 036402.

(142) Smeets, E. W. F.; Voss, J.; Kroes, G.-J. Specific reaction parameter density functional based on the meta-generalized gradient approximation: application to H_2 + Cu(111) and H_2 + Ag(111). *J. Phys. Chem. A* **2019**, *123,* 5395–5406.

(143)   Ghassemi, E. N.; Somers, M. F.; Kroes, G.-J. Assessment of two problems of specific reaction parameter density functional theory: sticking and diffraction of H$_2$ on Pt(111). *J. Phys. Chem. C* **2019**, *123*, 10406–10418.

(144)   Díaz, C.; Olsen, R. A.; Busnengo, H. F.; Kroes, G. J. Dynamics on six-dimensional potential energy surfaces for H$_2$/Cu(111): Corrugation reducing procedure versus modified Shepard interpolation method and PW91 versus RPBE. *J. Phys. Chem. C* **2010**, *114*, 11192–11201.