Hydrogen dissociation on metal surfaces

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CHAPTER 1

Introduction

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1.1 Reactions of molecules on surfaces

A large number of processes in chemistry and physics, both in everyday life and in industry, occur at a surface. Atoms and molecules can interact with a surface, but also light and heat can. Well known examples of surface chemistry in everyday life are for example the rusting (oxidation) of metals and the conversion of toxic exhaust gases of a car into less harmful gases. An example from physics is the transfer of heat through a surface, which is noticeable in everyday life by the air inside a house cooling down on a cold day, but also by a lake freezing over, which starts at the water–air surface and then continues downward.

Processes occurring at surfaces are also heavily used in industry. Probably the most famous industrial process making use of surface chemistry is the Haber–Bosch process,[1]

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

the process in which ammonia is synthesized, an important chemical in the production of fertilisers, which are needed in order to produce food for the world population. Another example of such a reaction is the methane steam reforming process,[2]

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

which is currently the most used method to produce hydrogen, for example for use in fuel cells.

In both of these processes, the metal surface acts as a catalyst, which lowers the barrier to reaction. The gas reactants such as N_2 or CH_4 are passed over the solid catalyst, on which they are then adsorbed and the reaction can then take place. For the Haber–Bosch process, commonly iron- or ruthenium-based catalysts are used, whereas for the methane steam reforming process commonly nickel-based catalysts are used.

Clearly, processes occurring at surfaces are important and it should therefore not come as a surprise that such processes are well studied, both from an experimental and a theoretical perspective. Many such processes are however rather complex. Often surfaces are not well-defined or rather rough, or the surface is polluted with atoms or molecules that had already been adsorbed on the surface, thus making

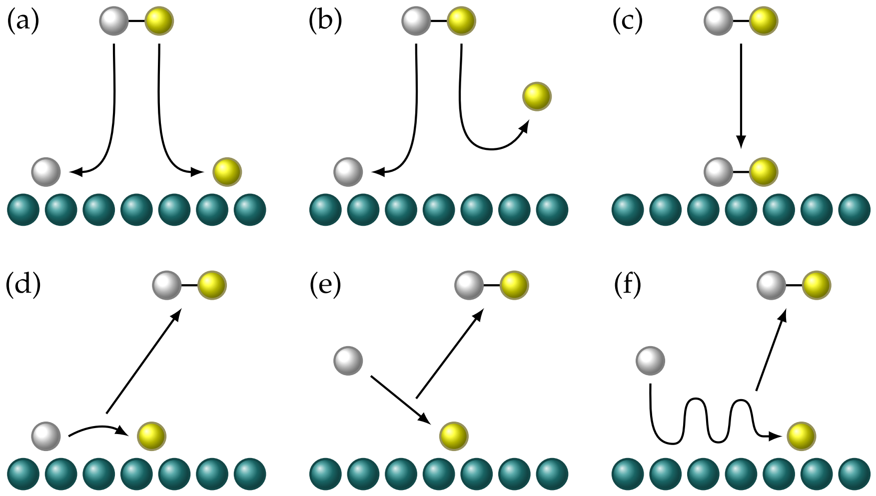

Figure 1.1 Different mechanisms for molecule–surface reactions: (a) dissociative chemisorption, (b) abstraction, (c) molecular adsorption, (d) Langmuir–Hinshelwood, (e) Eley–Rideal and (f) the hot-atom mechanism.

it unclear what causes a particular process to occur. It is even possible that such pre-adsorbed particles block a particular process from occurring. Often therefore well-defined surfaces are used, and a large number of studies in the field of surface science consider clean, single crystal-cut surfaces. This reduces the complexity of the system considerably and makes it possible to understand, at the very least in a qualitative way, processes at surfaces.

Research on molecule–surface reactions has revealed various mechanisms, the most common mechanisms being shown in figure 1.1. Before any chemistry can occur on a surface, first the surface needs to be covered with some reactant, *i.e.*, atoms or molecules. The way to achieve this is by adsorbing this reactant on the surface. In figure 1.1(a) to (c), three mechanisms are shown for a molecule being adsorbed to the surface: dissociative chemisorption (a), in which a bond of the incoming molecule is broken and both fragments are adsorbed to the surface; abstraction (b), in which a bond of the incoming molecule is also broken but only one fragment is adsorbed to the surface while the other fragment bounces back into the gas phase; and molecular adsorption (c), in which the molecule is adsorbed onto the surface as a whole, and no bond in the molecule is broken, either by chemisorption or physisorption.

It is also possible for molecules to combine with a fragment that is adsorbed on the surface and then dissociate. Three such mechanisms are shown in figure 1.1(d) to (f): Langmuir–Hinshelwood (d), in which two fragments that are adsorbed on the surface meet each other, form a new bond and dissociate; Eley–Rideal (e), in which a fragment coming in from the gas phase collides with an adsorbed fragment to form a new bond and the molecule formed in this way desorbs; and the hot-atom mechanism (f), in which a fragment from the gas phase collides with a surface, makes several bounces while it is not yet equilibrated with the surface, after which it collides with another adsorbed fragment on the surface, forming a new bond with this fragment, and the molecule formed in this way desorbs.

Of particular interest is the dissociative chemisorption mechanism, which is in many applications of molecule–surface reactions an elementary step in the reaction and can even be the rate-limiting step: for example, in the Haber–Bosch process, both N_2 and H_2 need to dissociate on the metal surface, and in this process N_2 dissociation is the rate-limiting step.[3]

1.2 Scattering of hydrogen from metal surfaces

As discussed above, an important step in many applications of molecule–surface reactions is the adsorption of (small) molecules on a metal surface. Understanding the scattering and adsorption of molecules on a surface is therefore often the first step to be studied for a chemical reaction occurring at a surface. An example of such a reaction is the scattering and adsorption of hydrogen molecules on a metal surface.

The scattering and adsorption of hydrogen molecules on a metal surface is a particularly interesting system to study. This is due to several reasons. A hydrogen molecule is a homonuclear diatomic molecule and thus it is the simplest system which can undergo dissociative chemisorption. Additionally, both thermal surface atom displacements due to phonons and electron–hole pair excitations, which can in principle occur, are expected to have a small effect on the dissociation of hydrogen on a metal surface.[4] For a discussion of these effects, and a detailed overview of theoretical results on H_2 dissociation on and scattering from metal surfaces, the reader is also referred to reviews on these topics, such as references 4–7.

For H_2 dissociation on Pt(111), it has been argued that electron–hole pair excitations should not play a large role in such a process.[8] For H_2 dissociation on Cu(111),[9,10] Cu(110)[11] and Ru(0001)[12] dynamical calculations have been performed in which non-adiabatic effects have been taken into account using electronic friction methods. No large non-adiabatic effects have been found in these calculations, suggesting that electron–hole pair excitations do not play a large role. Furthermore, for activated systems, the amount of energy exchanged between H_2 and the surface is not expected to be large,[13,14] due to the large mass mismatch between the H_2 molecule and a surface atom.[15,16]

By making these approximations it becomes computationally feasible to represent the potential energy surface (PES), as it only has six dimensions, as well as to perform many (quasi-)classical trajectory and quantum dynamics[4] calculations. This allows, for example, the effect the used electronic structure method has on the PES and through that on dynamical properties to be investigated.

1.2.1 The hydrogen molecule

Before the case of a hydrogen molecule interacting with a metal surface can be discussed, first the hydrogen molecule itself needs to be discussed. The hydrogen molecule is the simplest and lightest diatomic molecule (two electrons) that can be considered. A diatomic molecule in general has six degrees of freedom. Applying the rules of quantum mechanics to a diatomic molecule has several consequences. The vibrational motion (associated with one degree of freedom) of the molecule is quantised and is represented by the quantum number ν and has a particular vibrational zero-point energy (ZPE). The rotational motion (associated with two degrees of freedom) of the molecule is also quantised and is represented by the quantum numbers J and m_J (see figure 1.2). Translational motion (given by the three remaining degrees of freedom)

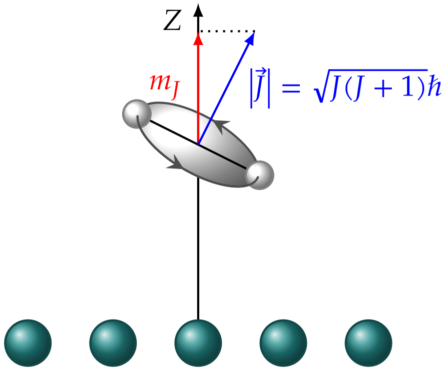

FIGURE 1.2 The angular momentum vector $\vec{J}$ of the hydrogen molecule together with its projection (m_J) on the surface normal (Z), and the definition of its angular momentum quantum number J.

is not quantised in the gas phase. The molecule can therefore have any amount of initial translational energy (E_{trans}) with any arbitrary incidence direction.

1.2.2 Hydrogen interacting with a surface

When a hydrogen molecule approaches a surface, the PES becomes more complicated due to the interaction of H_2 with the metal surface. If the surface is considered to be frozen, the PES will depend on the six degrees of freedom of the H_2 molecule. As the molecule approaches the surface, the bond will stretch and, if enough energy is present, the molecule may overcome the barrier to dissociation, and as a result two individual H atoms are adsorbed on the surface. If not enough energy is present in the H_2 molecule to overcome the barrier to dissociation, it may scatter back or it may stick on the surface without the molecule dissociating.

In any collision of a molecule with a surface, energy can be redistributed over the molecule from one degree of freedom to another, or the molecule can lose energy to the surface. In figure 1.3 these possibilities are shown for scattering of a diatomic molecule from a metal surface. In principle, any combination of these processes can occur when a molecule scatters on a metal surface. If no energy is rearranged over the

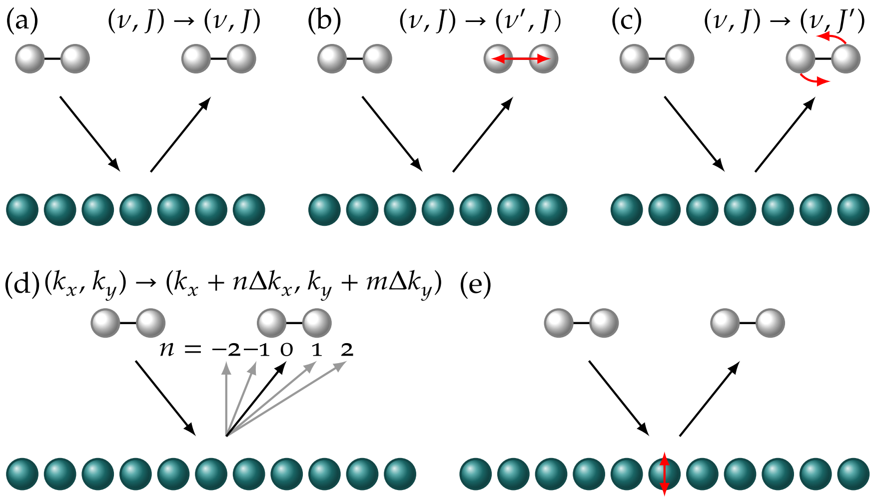

FIGURE 1.3 Scattering of a diatomic molecule on a metal surface: (a) elastic scattering, (b) vibrationally inelastic scattering, (c) rotationally inelastic scattering, (d) diffraction and (e) excitation of phonons.

molecular degrees of freedom, it is called elastic scattering (a). If energy is transferred into the vibrational or rotational degrees of freedom of the H_2 molecule, it is called vibrational inelastic scattering (b) or rotational inelastic scattering (c), respectively. Near a surface the momentum parallel to the surface can only change in discrete amounts due to the periodic nature of such a surface. This process is called diffraction or diffractive scattering (d). The associated quantum numbers are n and m, and the diffraction quanta are given by $\Delta k_x = 2\pi/L_x$ and $\Delta k_y = 2\pi/L_y$, respectively, with L_x and L_y the lengths of the surface unit cell. Finally, the molecule may also excite surface degrees of freedom, *i.e.*, phonons (e) and electron–hole pairs. It is noted that due to the quantisation of rotational, vibrational and parallel motion of the H_2 molecule, energy transfer from or into these degrees of freedom may only correspond to full energy quanta. For motion perpendicular to the surface, however, no such restrictions apply and any amount of energy can therefore be transferred into this degree of freedom. The surface degrees of freedom are in theory also quantised. Phonons show discrete states, and in electron–hole pair excitations electrons of the surface are excited into another state. Electron–hole pair excitations are, however, in infinitely sized metals possible with infinitesimally small energy changes because the highest band occupied by electrons is only partly filled.

Depending on the precise interaction of H_2 with the surface, different potentials are obtained. It is therefore of interest to define several different types of H_2–surface systems. From a phenomenological point of view, it is interesting to define different types of H_2–surface systems based on the interactions and, in particular, the barrier heights found in the PES of such a system. Such a system can show activated (barrierless) or non-activated dissociation. There are, however, also systems falling in between these two extrema, such as H_2 dissociation on Ru(0001)[17,18] and Pt(111).[8,19] It is therefore illustrative to make a division in three types of systems, in order of increasing probability for reaction: strongly activated systems, weakly activated systems and non-activated systems. It is emphasized that this division is somewhat arbitrary, especially considering that the scale might be somewhat continuous, considering that the barrier heights for different systems are in general different, and as such no two systems are equivalent. The three "model" systems are now briefly discussed, and examples are given.

Strongly activated systems show late, high barriers to dissociation for all possible geometries and therefore show the least amount of reaction of all cases. Examples of these systems include H_2 dissociation on Cu(111),[20] Cu(110),[20] Cu(100),[20] Ag(111)[21] and Au(111).[21] Molecules that have an energy high enough to overcome the barrier react, whereas molecules that do not have an energy high enough to overcome the barrier scatter back into the gas phase. The reaction probability as a function of collision energy generally rises monotonically up to the saturation value, as the H_2 molecule, with increasing incidence energy, can overcome the barrier to dissociation for more reaction pathways. For Cu(111),[22] Cu(100)[23] and Ag(111),[24] the lowest barrier is found for the bridge site.

On the other side of the spectrum are the systems with non-activated dissociation, in which at least some of the reaction pathways show no barrier. Other reaction pathways show barriers that can be either early or late. Examples of these systems include H_2 dissociation on Pd(111),[25,26] Pd(100),[27] Ni(110),[27] Ni(100)[27] and V(111).[28] Often, not all reaction pathways show barrierless dissociation, and the reaction probability still increases with increasing incidence energy. For low incidence energies, however, the reaction probability may also be increased due to the trapping of molecules in a well in the potential.[29,30] For Pd(111), barrierless dissociation is found for the top site.[30]

The weakly activated systems share properties with the strongly activated and the non-activated systems. No barrierless pathways are found, *i.e.*, dissociation is an activated process. Examples of these systems are H_2 dissociation on Ru(0001),[17,18] Rh(111),[31,32] Pt(111)[8,19] and Ni(111).[27] The PES only shows low barriers to dissociation and these are often early (far away from the surface), as found for Pt(111)[33] and Ru(0001).[17] As there is no barrierless dissociation, the reaction probability, as for the strongly activated systems, increases monotonically with increasing incidence energy. For Pt(111),[33] Ru(0001)[17] and Ni(111),[34] the lowest barrier is found for the top site.

1.2.3 Approximations and challenges

There are a number of approximations inherent to theoretical treatments of scattering of H_2 from metal surfaces and a number of challenges remain. First the approximations are considered. The three large approximations are:

- the ideal static surface approximation,
- the neglect of electron–hole pair excitations,
- the exchange–correlation (XC) functional used in density functional theory (DFT).

In the ideal static surface approximation, the surface atoms are assumed to be frozen in their ideal lattice positions (after the surface is allowed to relax), and as a result neither energy exchange between the molecule and the surface, nor the effect of the increased corrugation of the surface due to the surface temperature is considered. It is also not possible for the surface to undergo expansion due to the surface temperature, which can have a marked effect on the reaction dynamics.[35] Additionally, from experiments on H_2 and D_2 desorbing from Cu(111), it is known that reaction probability curves broaden as a function of the surface temperature.[36,37]

The neglect of electron–hole pair excitations is the next approximation. When a molecule collides with a surface, it can excite electrons of the surface (*i.e.*, the Born–Oppenheimer[38] approximation does not hold). As crystals, due to their periodicity, exhibit a band structure and the highest occupied band in metals is only partly filled, for metal surfaces electronic excitations can occur with an infinitesimally small energy. This approximation thus seems dangerous for reactions of molecules on metal surfaces. For H_2 dissociation on metal surfaces however it has been argued[8] that electron–hole pair excitations do not have a large effect on reactive and non-reactive scattering. For H_2 dissociation on Cu(111),[9,10] Cu(110)[11] and Ru(0001)[12] electronic friction-based approaches have been used to study non-adiabatic effects in dynamical calculations. No large non-adiabatic effects have however been found in these calculations, suggesting that this approximation is not bad for reactions of H_2 and D_2 on metal surfaces.

The XC functionals used in DFT calculations on molecule–surface reactions are not exact and as the generation of the PES depends on the DFT calculations, the PES is therefore not exact. The approximations used in the construction of the XC functionals therefore also pose limits to the accuracy of a description of a molecule–surface reaction. For molecule–surface reactions, commonly generalized gradient approximation (GGA)[39,40] level functionals are used as these are readily available in many quantum chemistry software packages. The local density approximation (LDA)[41] does not work well for molecule–surface reactions,[42–44] as it tends to give barriers for activated processes that are significantly too low compared to experimental data. The levels of approximations for the XC functional are further described in section section 2.2.1.

Apart from the approximations given above, also challenges remain for molecules reacting on metal surfaces in general[45,46] which are not all immediately related to reactions of H_2 on a metal surface. One such challenge is the treatment of more complex systems. For example, the dissociation of CH_4 and its isotopologues on metal surfaces have recently been studied using *ab initio* molecular dynamics (AIMD) calculations,[47] and also the dissociation of N_2 on W(110) has recently been studied.[48] Although N_2 dissociation does not introduce any additional degrees of freedom, energy exchange with the surface is a more important process as the mass mismatch between a N_2 molecule and a metal atom is not as small as it is for a H_2 molecule with a metal atom. Additionally, whether electron–hole pair excitations might have a large effect on reaction of N_2 on W(110) and other metal surfaces remains a matter of debate.[11,45,49]

The surface can also be made more complex, for example by adding pre-adsorbed atoms or molecules to it or considering surface cuts which exhibit a lower symmetry and a larger unit cell, such as stepped surfaces. Adding pre-adsorbed atoms or molecules is rather interesting because these types of systems can be examples of the "poisoning" of a catalyst. Each of these changes makes a treatment using a static model more complex and as such the use of AIMD is an interesting approach.[50]

1.3 Scope and aim of this thesis

As discussed above, there are a number of commonly used approximations and limitations to theoretical descriptions of surface science. In this thesis, the main aim is to provide an improved description of H_2 dissociation on metal surfaces, and to better understand when and why the approximations discussed above fail. Predominantly the effect of the XC functional is considered (chapters 4 to 7), but attempts are also made to go beyond the ideal static surface approximation (chapters 3 and 7) and to include adsorbates on the metal surface (chapter 7).

In **chapter 2** the theory of the dynamical methods used in this thesis is described. Also an overview of DFT is given, as well as an overview of the interpolation method used for the PESs in the later chapters of this thesis, the corrugation reducing procedure (CRP).

In **chapter 3** a model is developed to describe surface temperature effects for the dissociation of H_2 and D_2 on Cu(111). In this model, in contrast to many models developed before, such as the (modified) surface oscillator (SO) models,[13,51–56] the goal is not to describe energy exchange, which may be expected to be a relatively small contribution to the dynamics because of the large mass mismatch between H_2 and Cu, but instead to describe the effect of the surface becoming more corrugated by the displacement of Cu atoms with respect to their ideal lattice positions at a particular T_s.

In **chapter 4** the XC functional dependence of the dissociation of H_2 on Ru(0001) is investigated to investigate whether a functional can be found which can describe the dependence of reaction on the incidence energy as well as the probability for diffraction. Various XC functionals are tested, including the revTPSS meta-generalized gradient approximation (meta-GGA) and functionals containing vdW-DF[57] or vdW-DF2[58] correlation.

In **chapter 5** the XC functional dependence of the dissociation of H_2 on Pd(111) is investigated, in order to investigate whether a better functional, possibly using vdW-DF correlation, can be found to describe this system.

In **chapter 6** the differences between the SRP48 and optPBE-vdW-DF functionals are investigated using quasi-classical dynamics calculations on the dissociation of H_2 on Cu(111), Cu(100), Ru(0001) and Pt(111) surfaces, in order to investigate whether functionals with vdW-DF correlation, here represented by optPBE-vdW-DF, can in principle provide an improved description of H_2 dissociation on metal surfaces compared to ordinary GGA functionals, here represented by SRP48.

In **chapter 7** the dissociation of D_2 on CO-covered Ru(0001) is investigated using an AIMD approach, in which special attention is paid to the effects arising due to the motion of CO and the Ru atoms.

1.4 Main results

Throughout this thesis various H_2–surface systems are considered. The main results of each chapter are discussed here.

CHAPTER 3: Static surface temperature effects on the dissociation of H_2 and D_2 on Cu(111)

In chapter 3, the surface temperature dependence of H_2 dissociation on Cu(111) is discussed using a static corrugation model, in which a pair potential is used to correct the PES for displacements of surface atoms.

In such a model energy exchange is not possible. The experimentally observed broadening[36] of the reaction probability as a function of incidence energy is attributed primarily to the displacement of surface atoms and can be described in at least a semi-quantitative way. The rotational quadrupole alignment parameter is decreased, especially at lower incidence energies, resulting in a better agreement with experimental data. For low surface temperatures, *i.e.*, at $T_s = 120\,\mathrm{K}$, which was used for the experimental molecular beam experiments, no large differences are observed with the ideal static surface calculations.

Chapter 4: The effect of the exchange–correlation functional on H_2 dissociation on Ru(0001)

In chapter 4, various XC functionals are tested for their applicability to the dissociation of H_2 on Ru(0001). For this system the energetic corrugation is known to vary with the XC functional used.[17] It is found that XC functionals which contain vdW-DF or vdW-DF2 correlation give a PES with a higher energetic corrugation for a particular lowest barrier height than the purely semi-local XC functionals that have been tested. As a result of this higher energetic corrugation, the reaction probability curves are broader for these functionals and thus are in better agreement with the width of the reaction probability curve measured in experiments. The revTPSS meta-GGA functional does not give a large improvement over the "standard" GGA functionals, *e.g.* those containing PBE correlation, but the meta-GGA does give a lattice constant in good agreement with experiments, in contrast to the standard GGA functionals. The PBE-vdW-DF2 functional, which combines PBE exchange with vdW-DF2 correlation, and the PBE:RPBE(50:50)-vdW-DF functional, which combines 50% PBE and 50% RPBE exchange with vdW-DF correlation, both give a good overall agreement with the experimentally measured reaction probabilities. These functionals however do not give a good agreement for diffraction, as the computed diffraction probabilities are too large compared to the experimental values. It is not fully understood why this is the case. This may be related to the Debye–Waller extrapolation, which was done by the experimentalists to estimate diffraction probabilities for a 0 K surface. It is unclear whether this extrapolation works well for this system.

Chapter 5: Towards a specific reaction parameter density functional for reactive scattering of H_2 from Pd(111)

In chapter 5, four XC functionals are tested on the dissociation of H_2 on Pd(111), in order to determine whether a specific reaction parameter (SRP) functional can be found for this system. A comparison with experimental data is complicated by the amount of experimental data available, as three different molecular beam experiments have been carried out and all three show different results. The latest experiment is assumed to be the most accurate. The PBE-vdW-DF functional is found to give a good agreement with the experimentally measured sticking probabilities above a collision energy of 125 meV. Below this energy, neither quantum nor quasi-classical dynamics can reproduce the experimental sticking probabilities, as the "upturn" of reaction probabilities for low incidence energies does not occur. The agreement with the experimentally measured state-resolved reaction probabilities, which have been measured at incidence energies lower than 125 meV, is also not good due to the lack of the upturn. The agreement between quantum and quasi-classical dynamics is however rather good in general. A reason for the lack of the upturn could be a lack of pathways in which barrierless dissociation can occur. It is also possible that the lack of energy exchange between the molecule and the surface in the dynamical model is responsible for the poor agreement with experiment. Calculations[14,59] on the H_2/Pd(111) system suggest that at low collision energies energy exchange with the surface might lead to trapping, which can in turn promote reaction.

Chapter 6: Performance of a non-local van der Waals density functional on the dissociation of H_2 on metal surfaces

In chapter 6, the optPBE-vdW-DF and SRP48 functionals are compared to each other with respect to the application to the dissociation of H_2 and D_2 on Cu(111), Cu(100), Pt(111) and Ru(0001). The PESs for the different systems are qualitatively similar for the optPBE-vdW-DF functional and the SRP48 functional. The potential as a function of the molecule–surface distance Z rises more quickly for the optPBE-vdW-DF functional than it does for the SRP48 functional. Both functionals give a good description of dynamical properties such as sticking probabilities, although the optPBE-vdW-DF functional gives a better overall description. Reaction probabilities for D_2 dissociation on Ru(0001) and Pt(111) computed with the optPBE-vdW-DF functional rise less quickly with increasing incidence energy than those computed with the SRP48 functional, causing the better agreement with experiment. The vibrational efficacy for H_2 dissociating on Cu(111) is slightly larger for the optPBE-vdW-DF functional. The dependence of reaction on the initial rotational quantum number J is different for the two functionals: the optPBE-vdW-DF functional predicts reaction to not or only slightly depend on J for small J, but the SRP48 functional shows a larger dependence on J (increasing with J also for small J, which is in disagreement with experiment). The computed rotational quadrupole alignment parameters are lower for SRP48, consistent with the higher reaction probabilities for this functional. Overall, the optPBE-vdW-DF functional gives results in better agreement with experiments than the SRP48 functional does.

CHAPTER 7: *Ab initio* molecular dynamics study of D_2 dissociation on CO-precovered Ru(0001)

In chapter 7, the dissociation of D_2 on a CO-covered Ru(0001) surface is considered. For this system, the AIMD method is used with the PBE-vdW-DF2 functional in order to incorporate the motion of the CO molecules and the ruthenium surface atoms. Two simulation cell sizes are considered: a 3×3 cell and a smaller $\sqrt{3} \times \sqrt{3}$ cell. The reaction probability at $E_{\text{trans}} = 0.466\,\text{eV}$ is about 0.05 higher for the 3×3 simulation cell than for the smaller cell. The reaction probabilities obtained with the PBE-vdW-DF2 functional are in good agreement with previously computed reaction probabilities with the RPBE functional, where no surface motion was taken into account. No large differences for the reaction probability are found between an ideal CO/Ru(0001) surface and a 180 K surface. A large amount of energy transfer to the CO molecules is found regardless, and the amount depends on the size of the simulation cell chosen. At $E_{\text{trans}} = 0.466\,\text{eV}$, $0.105 \pm 0.002\,\text{eV}$ is transferred to the surface for a $\sqrt{3} \times \sqrt{3}$ simulation cell, while $0.263 \pm 0.007\,\text{eV}$ is transferred to the CO molecules and the surface for a 3×3 simulation cell. Energy transfer occurs mostly to the lateral degrees of freedom of the CO molecule. Energy transfer involving motion perpendicular to the surface occurs mostly when a molecule collides head-on with the CO molecule, which is not dependent on the simulation cell size. As the D_2 molecule can move into the CO layer, the difference in energy exchange for the lateral degrees of freedom is caused by the molecule pushing against mirror images in such a way that the forces working on the CO molecules partially cancel each other for smaller simulation cells. This results in a decreased amount of energy which is exchanged with the surface and CO molecules. The energy that is exchanged with the CO molecules causes the molecules to move apart, locally "opening" the surface, making it more favourable for reaction of D_2 to occur.

1.5 Outlook

Although many questions are answered by this thesis, also many new questions and ideas arose as a result of the research carried out in this thesis. In this section these questions and ideas are described and discussed.

First of all, there are several questions related to the performance of XC functionals for molecule–surface reactions. The performance of higher level DFT calculations, based on for example meta-GGA or hybrid XC functionals, is still unclear. In particular meta-GGA calculations are interesting, because functionals are available that give both a good description of the molecule–surface interaction as well as the surface itself.[60] It is, however, not yet clear how adding a van der Waals correction by combining vdW-DF or vdW-DF2 correlation with a meta-GGA exchange functional would affect the PES and dynamics of molecule–surface systems. Furthermore, it is in general not yet fully clear how large the error of GGA functionals is for barrier heights of molecule–surface systems, nor is it fully clear how this translates into errors in dynamical properties. Only for reaction probabilities this is immediately apparent: a too high barrier height generally results in too low reaction probabilities, and *vice versa*. More complicated dynamical properties, such as vibrational efficacies or inelastic scattering probabilities may be more sensitive to more detailed properties of the PES. In order to get an idea of the sensitivity of these detailed properties, these properties should be investigated for one or more H_2–surface systems for several functionals, including those which give similar reaction probabilities, so that the effect of a wrong barrier height can be mostly eliminated. Also interesting is to check the performance of the optPBE-vdW-DF functional used in chapter 6 for other molecule–surface systems, and to check whether better functionals can be found.

Second, the discrepancies found between experiment and theory for both H_2 dissociation on Ru(0001) (chapter 4) and Pd(111) (chapter 5) suggest that either the theoretical description is incomplete or that the experimental results are not rightly interpreted. For H_2 on Ru(0001), the reported experimental diffraction probabilities could not be reproduced by theory, while the reaction probability could be. This may be related to the Debye–Waller extrapolation used by experimentalists to extrapolate their diffraction probabilities at elevated surface temperatures to $T_s = 0\,\text{K}$ in order to compare to theoretical results. For H_2 dissociation on Pd(111), rather different experimental values are reported in the literature for the reaction probability. Although one can assume the latest experiments to be the most accurate, this is not a given and new experiments, preferably with a good characterisation of the molecular beam, should be performed on this system to validate the previous experiments. On the side of theory, it might also be useful to perform quantum dynamics for more XC functionals in order to validate whether the upturn observed for reaction at low collision energies can be reproduced. Additionally, one could explore whether allowing energy transfer to the surface alters the results, as energy transfer to the surface may affect non-activated dissociation quite differently than activated dissociation, for instance by promoting trapping mediated dissociation.[7,14,59]

Third, a better understanding is needed for the dissociation of D_2 on CO-covered Ru(0001) (chapter 7). Although energy exchange with the surface plays an important role in the dissociation dynamics, the effect it has on the reaction probability is not large enough to explain the full difference between the present theory and the experiments. Using a larger simulation cell causes more energy to be exchanged with the surface and the reaction probability to increase somewhat. There are several possible reasons for the discrepancies between theory and experiment: (i) it is not yet fully clear whether the larger unit cell currently used is large enough to capture all possible effects; (ii) the experimental structure and coverage of CO on the surface may not precisely match to the theoretical structure and coverage; (iii) the effect of electron–hole pair excitations may be bigger than expected for this system; or (iv) the XC functional is not quite right for this system, even though it worked well for D_2 dissociation on bare Ru(0001). Of particular interest to theory are reasons (i) and (iv): calculations can be performed in a rather straightforward way to see whether they apply. For (i), AIMD calculations could be done on a larger simulation cell and compared to the present results. For (iv), calculations could be done using a different XC functional. It is noted however that changing the XC functional can fix most discrepancies, regardless of the origin of those discrepancies, possibly masking the relevant physics. It is therefore still needed to test whether the other reasons might apply.

Finally, it is noted that it is relatively easy to extend the static corrugation model of chapter 3 to other metal surfaces. Such an extension would allow surface temperature effects to be studied in other H_2–surface systems. Additionally, it may be of interest to perform quantum dynamical calculations for H_2/Cu(111) or other systems using a vibrational sudden approximation, in which various random geometries and thus perturbations in the PES are introduced, after which the reaction or scattering probabilities are averaged over all selected geometries. Another interesting question is how large the role of energy exchange is for systems like H_2 dissociation on Cu(111) and what effect this has on dynamics, if any at all. Extending a static corrugation model such as detailed in chapter 3 to also include surface motion is an interesting possibility for such a study, as the effect of energy exchange can then be studied by displacing the surface atoms but fixing them in space and comparing this to the case where the surface atoms are displaced and allowed to move. The only modification that needs to be made to such a model is the addition of a strain term, which describes how the PES of the surface in absence of the H_2 molecule depends on the surface degrees of freedom.

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CHAPTER