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Dynamics of H₂ on Ti/Al(100) surfaces

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Dynamics of H₂ on Ti/Al(100) surfaces

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Jian-Cheng Chen

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To my parents

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Chapter 1

Introduction

1.1 Hydrogen production and storage

The world reserves of fossil fuels (oil, coal and natural gas) are limited, the peak of oil and natural gas production has already been reached. The depletion of current oil resources (heavy crude oil, oil sands, and oil shale are not counted as part of the oil reserves) is expected to take place in about 40 years, natural gas (including shale gas but without methane hydrates) in about 60 years and coal in about 200 years at the current usage rate [1, 2]. The importance of research aimed at enabling the introduction of hydrogen as a clean fuel can hardly be overstated. Scientific evidence is accumulating that human activity has increased the concentrations of atmospheric trace gases, e.g., CO_2 and CH_4 , which in turn has elevated global surface temperatures by blocking the escape of thermal infrared radiation [3]. In the Third Assessment Report, the Intergovernmental Panel on Climate Change (IPCC) projects an increase of mean global average temperature by 2-6 °C by the year 2100, relative to pre-industrial times [4–7]. The associated impacts of global warming not only have consequences such as a rise in sea level, more frequent heat waves, increases in rainfall, increases in frequency and intensity of many extreme climate events, but also have fingerprints on wild animals and plants in species ranging from molluscs to vertebrates and from grasses to trees [8].

One of the solutions to these challenges requires a switch to renewable energy technologies [6]. Using sunlight to split water into its components, hydrogen and oxygen, is one of the most promising and sustainable tactics to escape current dependence on coal, oil, and other traditional fuels. Combustion of hydrogen forms just water vapor without releasing carbon dioxide, the main greenhouse gas. Hydrogen is one of the few carbon-free energy carriers and can be stored for future use (nuclear fission fuels like uranium can cause disasters like the one in Fukushima, whereas nuclear fusion still seems to have a horizon of 50 years before commercialization). Beside serving as a fuel for

combustion engines, pure hydrogen can also be used to produce electricity through the proton exchange membrane (PEM) fuel cell, in which a semipermeable membrane is designed to conduct protons while being impermeable to the gases, oxygen and hydrogen [9]. However, the appeal of hydrogen-based energy or the so called *hydrogen economy*, with hydrogen as the major fuel, requires breakthrough solutions for the cost-effective production of hydrogen from renewable energy sources. On board storage of H₂ fuel has been identified as another primary challenge for the hydrogen economy [6, 7].

1.1.1 Hydrogen production

A number of emerging technologies such as water splitting using solar and nuclear heat, biomass gasification, photo-electrolysis and biological processes are also being developed, but are still far from being commercialized [10]. The current commercial process of hydrogen production still depends on the steam reforming of natural gas and gasification of coal. Both methods have the disadvantage of CO₂ emission. Hydrogen is mainly consumed as an intermediate for the Haber process of ammonia synthesis for agriculture fertilizer supply [10].

Systematic research towards practical implementations of a hydrogen economy has been set as a rigorous goal according to the International Energy Agency (IEA) report [10]. In 2003, the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) was established as an international institution to accelerate the transition to a hydrogen economy [11]. Each of the IPHE partner countries has committed themselves to accelerate the development of hydrogen and fuel cell technologies to improve the security of their energy supply, environment, and economy.

One of the ideas in current methods for H₂ production in photo-electrolysis is to replace the dominate silicon photovoltaic cells by a new generation of “Grätzel cell” based on nanocrystalline materials and conducting polymer films [12]. These offer the prospect of cheap and widely available materials, such as TiO₂, ZnO₂, SnO₂, Nb₂O₅ and CdSe, with attractive features. The Grätzel cell converts energy from the red part of the solar spectrum to electricity, providing the small extra bias to drive oxygen production over the metal-oxide electrode which absorbs blue light in the photoelectrochemical cell.

1.1.2 Hydrogen storage

Hydrogen is a gas at ambient temperatures. It has a critical temperature of -240 °C, and a low energy density per volume. These are among the main reasons why hydrogen is not the major fuel of today. Storage in gaseous form requires a too large volume for automotive use, and one third of the energy content of H₂ is needed to liquefy hydrogen [13, 14]. The most commonly quoted targets established by the United States Department

of Energy (DOE) for new materials for hydrogen storage are the weight and volumetric density [15]: By 2015, the goal is to develop and verify on-board hydrogen storage systems achieving 1.8 Wh/kg (5.5 wt %), 1.3 kWh/L (39 g/L).

A. Conventional metal hydrides storage

Conventional metal hydrides, e.g., $\text{PdH}_{0.6}$ [16] and LaNi_5H_6 [17], exhibit good thermodynamic properties for the H_2 charging and discharging processes. But the weight percentages in these metal hydrides are too low for on-board applications. Conventional high capacity metal hydrides require high temperatures to liberate hydrogen.

B. Complex metal hydrides

Although LiAlH_4 is metastable at room temperature, its partial dehydrogenation process from LiAlH_4 to LiH still needs 200 °C with a H_2 weight percent of 7.9 wt % [18]. Hydrogen storage in MgH_2 often uses Pd or Ti membranes to dissociate H_2 , then atomic-H diffuse through the membranes to the Mg layer [19]. Hydrogen release in MgH_2 takes place at 300 °C [20]. The system of LiBH_4 requires even a higher temperature of 400 °C to be decomposed into LiH and B. In transportation applications, sufficient heat is not generally available because the high performance heat exchangers would add extra weight to the on-board systems. The related AlH_3 system contains up to 10 % hydrogen by weight, corresponding to 148 g/L, twice the density of liquid H_2 . Unfortunately, AlH_3 is not a reversible carrier of hydrogen.

Another system that comes closest to meeting practical requirements is the sodium alanate (NaAlH_4) system. The theoretical reversible storage capacity of NaAlH_4 is about 5.5 wt %. A key point is that the release and re-uptake of H_2 can be made reversible by adding a catalyst like Ti, as demonstrated in 1997 by Bogdanovic and Schwickardi [21].

C. Alkali amidoborane

Ammonia borane, NH_3BH_3 , has received significant attention because of its reported release of 12 wt% hydrogen at moderate temperatures (150 °C). However, the hydrogen purity suffers from the release of trace quantities of borazine [22]. Recent research shows that reacting alkali or alkali earth metal hydride (LiH , NaH , or CaH_2) with amidoborane (AB) produces amidoborane with improved dehydrogenation properties [22]. Lithium amidoborane (LiAB), sodium amidoborane (NaAB) [22] and calcium amidoborane (CaAB) [23], can release 10.9 wt%, 7.5 wt% and 8.0 wt% of H_2 at moderate temperatures, respectively. It was observed that hydrogen desorption from those amidoborane

ammonites started at temperatures below 70 °C and more than 8.0 wt% of H₂ can be released at 150 °C without borazine emission.

D. Water and ammonia borane clathrate hydrates

Water clathrate hydrates are cage-like crystalline compounds formed by water hydrogen-bonds. There are two common clathrate hydrate structures: sI and sII. The sI hydrate has two small 5¹² cages and six larger 5¹²6² cages per unit cell. The sII hydrate has sixteen 5¹² cages and eight 5¹²6⁴ cages per unit cell [24]. At an extremely high pressure, 220 MPa and -24 °C, hydrogen clusters can be stored in the clathrate hydrate cages with a H₂/H₂O molar ratio of 1:2 [25]. Promoted water clathrate hydrates [26] by tetrahydrofuran (THF) can be stabilized at pressures as low as 5 MPa.

Analogous to the water clathrate hydrates, another proposed system, ammonia borane clathrate [27] has been studied theoretically for hydrogen storage by lowering the temperature down to -196 °C at ambient pressure.

E. Metal-organic frameworks

Metal-organic framework (MOF) [28] is a cubic three-dimensional extended porous structure, with a composition of Zn₄O(BDC)₃ (BDC = 1, 4 - benzenedicarboxylate). MOF can adsorb hydrogen up to 4.5 wt % at - 195 °C and 1.0 wt % at room temperature and a pressure of 20 bar [28]. MOF still shows a too low weight percentage of H₂ at near ambient conditions.

F. Organometallic buckyballs

Transition metal (TM) atoms bound to fullerenes (C₆₀ or C₄₈B₁₂) have been proposed as absorbents for high density, room temperature, ambient pressure storage of hydrogen [29]. Particularly, organometallic buckyballs (OBBs) may work well if scandium is used. Scandium OBB can bind as many as 11 hydrogen atoms per TM, ten of which are in the form of molecular hydrogen that can be adsorbed and desorbed reversibly. In this case, the calculated binding energy is about 0.3 eV / H₂, which is ideal for use on board vehicles. The theoretical maximum retrievable H₂ storage density is 9 wt% [29]. However scandium is too expensive for this to be of practical use.

G. Other materials

Adsorption on carbon nano-tubes only leads to reasonable weight percentages of adsorbed hydrogen at liquid nitrogen temperatures [30, 31]. Ammonia (NH₃) produced from the

Haber process can be used for chemical hydrogen storage. NH₃ is a liquid at - 33 °C at ambient pressure or at 25 °C at 10 bar [32]. It has a high hydrogen weight percent of 17.7 wt %. Unfortunately, the Haber process itself is energetically expensive.

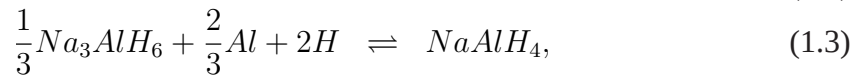
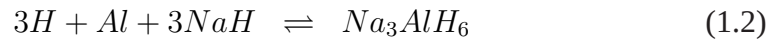
Focus in this thesis

As the sodium alanate system is one of the more promising and well studied systems I have chosen to focus on aspects related to this system in my thesis. In particular, I will study the dynamics of the elementary reaction $H_2 \rightleftharpoons 2H$ with the aim to better understand the catalytic role played by Ti in NaAlH₄.

1.2 H₂–surface reactions

It is well known that many chemical reactions involve surface reactions. Breathing (oxygen transport from the air to our blood), stains (rust) forming on a bicycle, the process of washing clothes in water using a detergent, ozone depletion on ice surface in the antarctic stratosphere [33], the most abundant molecule in the universe – H₂ – forming on surfaces in the interstellar medium (of dust particles of silicates, graphite, and other carbonaceous compounds) [34], are all examples involving surface reactions.

The hydrogen storage process in NaAlH₄ can, in principle, be envisaged to take place through the following three steps,



which can be summarized as,



Recent isotope exchange experiments [35] on both absorption and desorption of H₂ in Ti-doped NaAlH₄ suggest that diffusion of heavier hydrogen-containing species, such as AlH_x or NaH, represents the rate limiting step in H₂ release and uptake. However, it seems likely that Ti should also catalyze H₂ dissociative adsorption (and the reverse process, associative desorption). The hydrogen-deuterium exchange and scrambling experiments [35–37] in NaAlH₄ have shown that the H/D exchange is much faster than the rehydrogenation of Ti-doped sodium alanate. The production of atomic hydrogen from gas phase H₂ should not be the rate limiting step in the process of (re-)hydrogenation.

From the evidence that H/D exchange does not take place when there is no Ti-doping [36], H₂ dissociation is most likely the rate limiting step in the H/D exchange process leading to HD formation. It is obvious that Ti atoms play a role to catalytically accelerate the breaking and forming of the H-H bond.

Low-energy electron diffraction (LEED) experiments by Kim *et al.* [38] show that, at low Ti coverage, Ti atom deposition on a clean Al(100) surface results in a $c(2 \times 2)$ pattern, with the Ti atoms probably residing in the second layer of the substrate. Low-energy ion scattering (LEIS) measurements by Saleh *et al.* [39] confirm that up to 1/2 ML Ti coverage, the surface Al atoms do indeed float on top of the Ti film, because the initial Ti deposition does not change the LEIS results. When the Ti coverage is increased further, Ti adatoms are incorporated also into the top layer of the Al substrate. For instance, the fact that half of the Al LEIS peak area remains after 2 ML Ti deposition [40], together with the LEED experiments [38], suggests that in this case a $c(2 \times 2)$ -Ti/Al(100) surface alloy is formed, in which half of the top layer is composed of Ti atoms.

These experimental studies provide a background for theoretical investigations of the catalytic role of Ti atoms in the process of H₂ dissociation on $c(2 \times 2)$ -Ti/Al(100) surfaces. This is the focus of my thesis.

1.2.1 Gas–surface reaction mechanisms

Catalysis can roughly be divided into two groups. The first one is homogeneous catalysis, in which the catalyst and reactants are in the same phase. The second group is heterogeneous catalysis, in which the catalyst and the reactants are in the different phases. The latter one is more widespread in industry, where the catalyst is usually a metal surface and the reactants are usually in the gas phase. The amount of surface area of the catalyst, its structure, and its composition determine the reactivity and the outcome of the reaction. H₂–surface reactions belong to the second group.

Most gas–surface reactions take place between chemisorbed reactants in thermal equilibrium with the surface. This is the *Langmuir-Hinshelwood* (LH) mechanism (*associative desorption*) [42, 43], see Fig. 1.1(a). Another one is the *Eley-Rideal* (ER) mechanism involving the direct impingement of an atom or molecule on a chemisorbed species resulting in immediate formation of the product and subsequent desorption to the gas phase [44, 45], see Fig. 1.1(b). These two mechanisms represents two “extreme” limits. When an atom or molecule collides with a surface, it may be trapped or be scattered back into the gas phase. A trapped atom or molecule could rebound many times before reacting with a pre-adsorbed atom or molecule and this process is called the *Harris-Kasemo* (HK) or *hot-atom mechanism* [41, 46], see Fig. 1.1(c).

In addition to the three desorption mechanisms for a product leaving a surface back to the gas phase, there are also three kinds of adsorption mechanism to break a gas phase

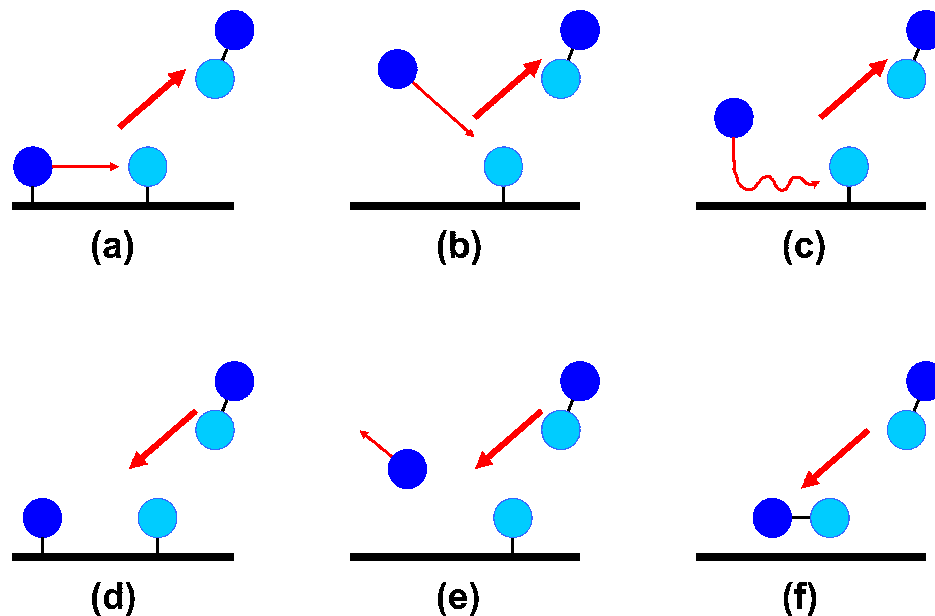


Figure 1.1: Illustration of the Langmuir-Hinshelwood mechanism (a), the Eley-Rideal mechanism (b), the Harris-Kasemo mechanism (c), the dissociative chemisorption mechanism (d), the abstraction mechanism (e) and the molecule-surface adsorption mechanism (f). In the plot, the surfaces are represented by horizontal bold lines and the molecules are represented by two filled circles. Initial and final states are indicated by direction of arrows [41].

molecule into atoms. The first one is the so called *dissociative adsorption mechanism* through which the molecule is dissociated and form bonds to the surface. This reaction can be regarded as the reverse process of the LH mechanism, see Fig. 1.1(d). In the second mechanism, abstraction, the molecular bond is also broken, but with only one fragment bound to surface while the other one escapes to the gas phase. This is the reverse of the ER mechanism, see Fig. 1.1(e). The last mechanism is called *physisorption* or *molecular chemisorption*, depending on the strength of the molecule-surface interaction, see Fig. 1.1(f). The physisorption is characterized by weak Van der Waals forces (without significant electron transfer between the molecule and the surface, and it is highly non-directional). A typical energy of a physisorption state is less than 0.3 eV, while a chemisorption energy is 0.5 eV or more [47].

In the case of H_2 -surface reactions one sometimes encounters a combination of two or more of the mechanisms mentioned above. For example, H_2 dissociative chemisorption on Ni(100) [48], Pd(111) [49] and 1 ML Ti-covered Ti/Al(100) [50] show both direct

(dissociative adsorption) and indirect (preceded by physisorption or molecular chemisorption) reaction routes, due to the presence of a H₂ molecular adsorption well in front of the barrier. At low surface temperatures the reaction proceeds through a molecularly adsorbed intermediate, where the kinetics is determined by the barrier to dissociation referenced to the molecular adsorption well. The H₂ + Cu(100) [51] and H₂ + Pt(111) [52] systems are both example of reactions proceeding through a direct dissociative adsorption mechanism.

1.2.2 Scattering of H₂ on metal surfaces

In this thesis, we consider a diatomic molecule, H₂ interacting with a Ti/Al(100) surface, in which either half of the Al first-layer and third-layer atoms are replaced by Ti atoms to form a 1 ML Ti-covered $c(2 \times 2)$ structure, or half of the second Al layer atoms are replaced by Ti to form a 1/2 ML Ti-covered $c(2 \times 2)$ structure. The surface atoms are fixed at their equilibrium crystal lattice positions. The periodicity of the surface is constructed by repeating the surface unit cell in X and Y directions infinitely. In Fig. 1.2(a), the first-layer surface structure and the $(\sqrt{2} \times \sqrt{2})$ and (2×2) unit cells are shown.

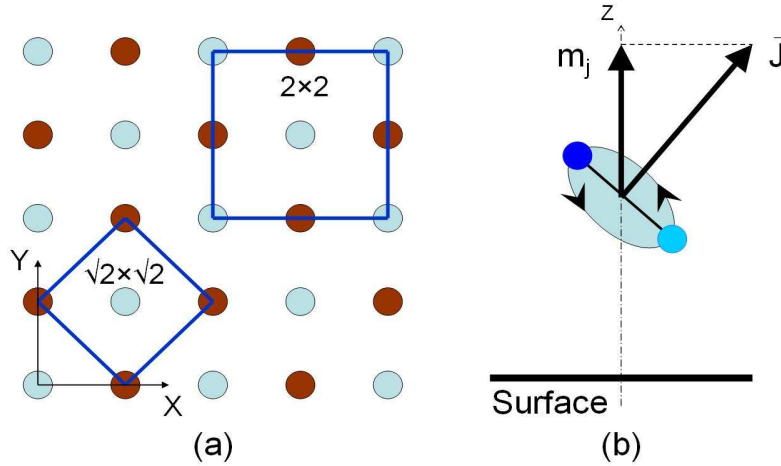


Figure 1.2: (a) Top view of the $c(2 \times 2)$ -Ti/Al(100) surface layer, in which brown and blue spheres represent Al and Ti atoms, respectively. The square area indicated by $(\sqrt{2} \times \sqrt{2})$ is the smallest repeating cell covering two atoms. Another larger square is a (2×2) unit cell covering four atoms. (b) Diatomic molecule (i.e. H₂) rotating with a total angular momentum vector $\mathbf{J}$ and its projection onto Z , m_j .

It is easy to understand that the interaction potential of the molecule on the surface is periodic, because translating the molecule from one unit cell to another without changing the relative position of the molecule in the unit cell will not change the interaction potential value. From the Bloch's theorem [53], the Hamiltonian with the periodic potential will

have periodic eigenfunctions. These periodic eigenfunctions indicate how the molecule can change momentum in the X and Y degrees of freedom, which is called *molecular diffraction*. The parallel momentum change in molecular diffraction is restricted to certain discrete amounts, *i.e.*, it can only take the discrete values $(k_X + m\Delta k, k_Y + n\Delta k)$. Here (k_X, k_Y) is the initial parallel momenta along X and Y . $\Delta k = 2\pi/L$ is the diffraction quantum for a square shaped surface unit cell defined by the lengths ($L_X = L_Y = L$). The integer numbers m and n are the diffraction quantum numbers. The case $n = m = 0$ is also called *specular reflection*. Experimentally, molecular diffraction was first observed in the early thirties by Estermann and Stern, in experiments on scattering of He and H₂ from a LiF(100) [54] surface.

The molecule moves towards the surface with an initial rotational motion. From quantum mechanics, there is a quantized angular momentum vector $\mathbf{J}$ perpendicular to the plane of rotation (see Fig. 1.2). The length of the vector $\mathbf{J}$ can only take on the values $\sqrt{j(j+1)}\hbar$, where j is the rotational quantum number, a positive integer or zero, and $\hbar$ is the reduced Planck's constant ($\hbar = h/2\pi$). In the center of mass frame, the rotational energy is given by $|\mathbf{J}|^2/(2\mu r^2)$, where μ is the reduced mass of H₂ and r is the H–H distance. In Fig. 1.2, the angular momentum vector $\mathbf{J}$ can be projected onto an arbitrary axis, usually choosing the direction normal to the surface (Z direction). The length of the projected vector is $m_j\hbar$, where m_j can only take on the integer values from $-j$ to j . The quantum number associated with the projected vector m_j is the magnetic rotational quantum number. For a particular j , there are a total number of $2j + 1$ allowed values of m_j . As a result of the collision with the surface, the molecular rotational state can change ($j, m_j \rightarrow j', m'_j$). Rotational (de-)excitation is closely related to the anisotropy of the molecule-surface potential. The higher the anisotropy, the more the molecule is likely to be reoriented in space when it gets close to the surface, and the larger the probability for rotational (de-)excitation becomes.

Vibrational excitation can also take place, but of course there must be enough (collisional or rotational) energy available to make this transition. In case of vibrational de-excitation, the vibrational energy can flow to other degrees of freedom. In quantum mechanics, only specific energies are allowed for the vibrational states v , a positive integer including zero. Here, $v = 0$ corresponds to the vibrational ground state and it has an vibrational zero-point energy of 0.27 eV for H₂ molecule. For vibrational excitation to take place to the first vibrational excited state enough energy must be made available from the collision to cover the gap between vibrational ground state ($E_{v=0,j=0} = 0.27$ eV) and the first vibrational excited state ($E_{v=1,j=0} = 0.78$ eV). The energy can e.g. flow from the translation motion to the vibrational mode, which is more likely if the minimum energy reaction path exhibits a significant curvature in front of the barrier, as is the case for the H₂ + Cu(111) system [55, 56].

1.2.3 Dissociation of H₂ on metal surfaces

The Ti/Al(100) alloy surface under our investigation involves the transition metal Ti atoms playing the role of a catalyst in the process of H₂ dissociation. The relevant orbitals to consider when studying the interaction of H₂ with a surface is the H₂ bonding state ϕ_{σ_g} , which is the symmetric linear combination of two atomic hydrogen 1s orbitals, and the H₂ anti-bonding state ϕ_{σ_u} , which is the corresponding anti-symmetric linear combination:

$$\phi_{\sigma_g}(\mathbf{r}) = c_1 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) + \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (1.5)$$

$$\phi_{\sigma_u}(\mathbf{r}) = c_2 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) - \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (1.6)$$

where the ϕ_s^H are the hydrogen 1s orbitals centered at the positions of the two hydrogen atoms $\mathbf{R}_1$ and $\mathbf{R}_2$, and c_1 and c_2 are the normalization coefficients [57, 58].

The bonding state is due to the overlap of the electronic orbitals between the nuclei, indicative of a net attractive force between the atoms. The electronic density between the nuclei of the anti-symmetric linear combination is zero, indicating a net repulsive force between the atoms. If the anti-bonding state of the H₂ molecule gets (partly) occupied during the approach to a surface, the molecule will tend to dissociate.

In metals, *i.e.*, titanium, aluminum or their alloy, the valence electron wave functions (4s, 3d orbitals for the Ti atom, 3s, 3p orbitals for the Al atom) at one site have significant overlap with those at the nearest neighbor sites. The conduction band is formed by this “sea” of valence electrons. The overlap between the conduction and valence bands allows electrons to move freely. When a gas phase H₂ approaches the Ti-alloyed Ti/Al(100) surface, the matchable energy level and spatial size between the H₂ bonding state ϕ_{σ_g} and Ti d_{z^2} state makes the H₂ bonding state split into a broadened lower lying ($\phi_{\sigma_g} - d_{z^2}$) bonding state and another higher-lying unoccupied ($\phi_{\sigma_g} - d_{z^2}$)_u anti-bonding state. Meanwhile, the H₂ anti-bonding state ϕ_{σ_u} and Ti d_{xy} state are matchable with each other and form a lower lying ($\phi_{\sigma_u} - d_{xy}$) bonding state and a higher lying ($\phi_{\sigma_u} - d_{xy}$)_u anti-bonding state. Due to the presence of a lower lying ($\phi_{\sigma_u} - d_{xy}$) bonding state the electrons start to fill the original gas phase ϕ_{σ_u} state, resulting in the H–H distance being elongated and finally in the breaking of the bond, *i.e.* dissociative chemisorption.

Although the H₂ molecule can also dissociate on an Al site of the Ti/Al(100) surface, the lack of the favorable ($\phi_{\sigma_u} - d_{xy}$) interaction results in a higher reaction barrier. The Ti atom on the Ti/Al(100) surface is therefore very favorable and selective towards H₂ dissociation.

The metal surface has a crystal structure and the surface atoms vibrate about their equilibrium positions. The motion can be regarded as that of harmonic oscillators at a finite temperature with an energy of $\varepsilon_n = (n + 1/2)\hbar\omega$. The vibrational modes can propagate in the whole crystal as a collective motion of ions [59]. The modes can be excited arbitrarily by heating or hitting the surface, *e.g.*, by colliding molecules. These

vibrational modes are called *phonons*. Unlike electrons, the phonons are bosons: their total number is not fixed, nor is there a Pauli exclusion principle governing the occupation of any particular phonon state.

In addition to the molecular transitions described above [diffraction, rotationally and vibrationally inelastic scattering and dissociative adsorption], it is also possible that energy is exchanged with the vibrations in the crystal surface (phonons) or with the electronic degrees of freedom of the surface (electron-hole pair excitations).

Often it is a good approximation to neglect the two latter processes. Phonon-inelastic scattering is certainly important in (rotationally inelastic) diffraction, but the effect of it can often be taken into account using the so-called *Debye-Waller* [60] factor. The Debye-Waller factor is the ratio of the coherent scattering or absorption cross section of a photon or electron by particles bound in a complex system to the value for the same process on an analogous free particle. It is often interpreted also as the probability of the coherent process, normalized to unity, with the difference of incoherent processes. The Debye-Waller factor is then interpreted as a measure of decoherence.

In the calculation of the dissociative chemisorption probability of molecular hydrogen on metal surfaces, the phonon-inelastic scattering and electronic transitions in the metal surface are negligible [60–62].

1.3 Scope and major results of this thesis

What is the catalytic role played by titanium in the hydrogen storage material NaAlH_4 [21]? This thesis aims at unraveling the dynamics of an elementary reaction: H_2 dissociation on $\text{Ti}/\text{Al}(100)$ surfaces. Although this reaction is not the rate limiting step in the hydrogen storage of NaAlH_4 , it is an important reaction to produce atomic hydrogen for the other reaction steps. To achieve the stated goal, we test a large set of possible slab models to represent the $\text{Ti}/\text{Al}(100)$ surface. After considering the stability of the slab model itself and the barrier height for H_2 dissociation, we carefully select two possible slab models: (1) the 1/2 ML Ti-covered $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ surface with Ti atoms in the second layer, (2) the 1 ML Ti-covered $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ surface with Ti atoms in the first and third layers [50]. Using these two slab models, potential energy surfaces (PES) are calculated. The H_2 dissociation probabilities and rate constants are then calculated. The results suggest that the 1 ML Ti-covered $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ surface may be the most realistic model for H_2 dissociation on $\text{Ti}/\text{Al}(100)$ surfaces relevant for the hydrogen storage material NaAlH_4 [50, 63, 64].

In **Chapter 1** (this chapter), the necessity of our research is presented from the aspects of the fossil fuels limitation and the impact of CO_2 on the global climate [1]. The main methods of hydrogen production and storage are summarized. We then focus on

one of the hydrogen storage materials, NaAlH_4 , and the relevant approach to gas-surface reactions that is used in this thesis.

Chapter 2 introduces the major methodologies used in this thesis. The Born-Oppenheimer (BO) approximation [65] and the Kohn-Sham single particle equation in density functional theory (DFT) [66, 67] are all essential elements in the application of this thesis to build the PESs. Two ways of PES construction methods are used: the Grow method [68–71] and the corrugation reducing procedure (CRP) [72, 73]. The H_2 dissociation probabilities are calculated by means of the pure classical trajectory (CT) and quasi-classical trajectory (QCT) methods, and a quantum dynamics approach employing the time-dependent wave packet (TDWP) method [51, 74–81]. The H_2 dissociation rate constants are obtained from transition state theory (TST) [82–86]. Using the QCT results, we also simulate the molecular beam experiments [87]: the curve of H_2 dissociation probability versus the beam nozzle temperature.

In **Chapter 3** we use DFT with the PW91 functional [88] to model Ti/Al(100) alloy surfaces and dissociation of H_2 on these surfaces, with a view to understanding the catalytic role of Ti and hydrogen release from and uptake in NaAlH_4 . Ti/Al surfaces were investigated with Ti coverages varying from 1/4 to 1 ML, with emphasis on $c(2 \times 2)$ structures modeling 1/2 and 1 ML coverages.

At 1/2 ML coverage, the energetically preferred $c(2 \times 2)$ structure (Model–2), with the lowest energy of Ti per Ti atom in Al, has the Ti atoms present in the second layer. At 1 ML coverage, the energetically preferred structure (Model–3), has the Ti atoms present in the first and third layers, again in a $c(2 \times 2)$ structure, with the Ti atoms in the third layer being underneath the Ti atoms in the first layer. In Model–2, the presence of Ti lowers the barrier for H_2 dissociation from 0.96 eV for a pure Al(100) surface (Model–1) to 0.63 eV. In Model–3, the presence of Ti lowers the barrier for H_2 dissociation even further, to only 0.23 eV, whereas the binding energy of Ti is higher by 0.23 eV/Ti atom than that in Model–2. Models with 1 ML and 1/4 ML coverages, with the Ti atoms present only in the first layer, have been found to exhibit even lower barriers to H_2 dissociation, but these show much higher binding energies for Ti in Al(100) slabs, and the Ti-Ti distances in these structures are in disagreement with the values obtained in Extended X-ray absorption fine structure (EXAFS) experiments. Because the Ti-Ti distance obtained with Model–3 is in excellent agreement with these experiments, and because Model–3 only exhibits a low barrier to H_2 dissociation, we conclude that this model probably represents the best model for describing Ti-catalyzed H_2 dissociation on Al(100) surfaces. With Model–3, H_2 dissociation is exothermic, and in the reaction path there is a molecular chemisorption well of depth 0.45 eV between the gas phase and the reaction barrier.

The two-center projected density [57, 58] of states analysis provides a molecular orbital view in which the barrier-less approach to the molecular chemisorption well is mainly explained by an occupied-virtual attraction between the H_2 σ_g and Ti $3d_{z^2}$ orbitals.

The barrier separating the molecular chemisorption well and the dissociated state can be understood as resulting from a competition between increasing overlap of the H_2 σ_u and Ti $3d_{xz}$ orbitals, and decreasing overlap of the H_2 σ_g and Ti $3d_{z^2}$ orbitals. It suggests that, to promote H_2 dissociation, the amount of Ti added should be high enough to provide, at least locally, a $c(2 \times 2)$ -Ti/Al(100) surface alloy with a Ti coverage of 1 ML, where Ti atoms are present in both the first and the third layers of the alloy surface.

In **Chapter 4**, also based on the DFT, we study the elementary reaction of H_2 dissociation on a 1 ML Ti covered Al(100) surface [63]. Firstly, the Grow method is applied to build a 6D electronic ground state PES using the BO and static surface approximations. H_2 dissociation probabilities are calculated through both the CT and QCT methods and the TDWP method. The dynamically interesting region is found to be at the Ti site of the surface where the molecular adsorption well in the MEP is located, leading to a high density of data points in this region with the Grow method. The MEP has been improved in the Grow PES. The new H_2 dissociation barrier is found to be only 0.13 eV, which is 0.10 eV lower than the one reported in our previous paper/chapter [50].

Using quasi-classical dynamics, we have calculated the dissociation probabilities for four initial quantum states of H_2 , *i.e.*: $(v = 0, j = 0)$, $(v = 0, j = 4, m_j = 0)$, $(v = 0, j = 4, m_j = 4)$, and the vibrationally excited state $(v = 1, j = 0)$. The dissociated trajectories for low incident energies (*i.e.*, below 0.20 eV) of the rovibrational ground state and the rotationally excited states have a relatively large number of rebounds from the surface (between 3 – 5), which indicates that these trajectories are trapped before dissociation. In contrast, the molecule in its vibrationally excited state dissociates more directly. Both rotational and vibrational excitation promote direct H_2 dissociation efficiently, with an efficacy of approximately 1.

The presence of the deep adsorption well in front of the barrier leads to statistical behavior: the H_2 dissociation probability depends only on the total (internal and translational) energy, except that the vibrational efficacy is somewhat larger than 1.0 in the low reaction probability region.

The reaction of H_2 in its rovibrational ground state $(v = 0, j = 0)$ is also considered using quantum dynamics. The calculations show that the QCT method describes the reaction more accurately than the CT method, as found earlier for most H_2 + metal surface systems studied.

In **Chapter 5**, we study the elementary reaction of H_2 dissociation on a 1/2 ML Ti covered Al(100) surface [64]. Firstly, the CRP method is applied to build a 6D electronic ground state PES using the BO and static surface approximations. The PW91 [88] and RPBE [89] functionals are employed to obtain the potential values respectively for the PESs. H_2 dissociation probabilities are calculated through both the CT and QCT methods and the TDWP method. We also carried out a molecule beam simulation and computed H_2 dissociation rate constants as a function of temperature.

H₂ dissociation on the 1/2 ML Ti/Al(100) surface has an activation barrier of 0.65 eV with H₂ dissociating from bridge to top site from the PW91 functional, and a barrier of 0.84 eV from the RPBE functional.

In the quasi-classical dynamics, we have calculated the dissociation probabilities for the following quantum states: $v = 0, j = 0 - 10$ and $v = 1, j = 0 - 7$, for both the PW91 and RPBE functionals. Adding translational energy is about 3.0 (1.6) more effective at promoting reaction than adding rotational (vibrational) energy.

The reaction of H₂ in its rovibrational ground state ($v = 0, j = 0$) and its vibrationally excited state ($v = 1, j = 0$) are also considered using quantum dynamics. The calculations show that the QCT method describes the reaction more accurately than the CT method, as found earlier for most H₂ + metal surface systems studied. The rate constants obtained from QCT results are larger than the TST ones.

In summary, based on the evidence that Ti plays a role in the process of hydrogen storage in NaAlH₄, in Chapter 5 we theoretically calculated the H₂ dissociation probability on the 1/2 ML Ti covered Ti/Al(100) surface. We hope that our predictions of the reaction probability curves can be confirmed by molecular beam experiments.

1.4 Outlook

Based on our results it seems likely that most of the Ti present in NaAlH₄ should be in a Ti-Al alloy form during cycling [90, 91]. Several experiments find Ti to be present in Al as a Ti-Al alloy of varying compositions [92–98]. Based on our DFT results, the elementary reaction of H₂ dissociation on a 1 ML Ti covered Al(100) surface [63] is believed to be the most realistic model for atomic hydrogen production. Although we have contributed some new insights into the first reaction step in Eq. 1.1, further questions in Eq. 1.2 and Eq. 1.3 concerning the dehydrogenation and rehydrogenation of NaAlH₄ have not been investigated in this thesis yet.

Recent ²⁷Al in situ NMR spectroscopy experiments [99] reveal that a mobile species (105 ppm) carrying both Al and H atoms at ambient temperatures could provide the large scale metal-atom transport needed for rehydriding. Isotope exchange experiments [35] on both absorption and desorption of H₂ in Ti-doped NaAlH₄ suggest that diffusion of heavier hydrogen-containing species, such as AlH_{*x*} (*x* can be 1 – 4) or NaH, represents the rate limiting step in H₂ release and uptake. However, the formation of AlH_{*x*} species, as well as the diffusion of AlH_{*x*} and NaH in NaAlH₄ are still not clear in large. Thus, further DFT investigations are necessary to investigate the formation of AlH_{*x*} on Al(100) surface and the diffusion of them into vacancies of NaAlH₄. The rate constant can be predicted through transition state theory (TST) and variational transition state theory (VTST) [82–86].

In our slab model studies, our six-dimensional potential energy surfaces are built with the Born-Oppenheimer (BO) [65] and static surface approximations. Although the static surface approximation has been shown to be a good approximation in systems like $\text{H}_2 + \text{Pt}(111)$ [60] and $\text{H}_2 + \text{Cu}(111)$ [62], the Ti and Al atoms are lighter than the Pt or Cu atoms. Thus, the interaction with surface phonons may not be negligible [100]. The applicability of the BO and static surface approximations in these (or similar) systems should therefore be investigated further. The surface oscillator model can be employed to describe the H_2 -surface coupling [61, 101, 102], in which the 9D PES $V_{9D}(\mathbf{R}_A; \mathbf{R}_B, \mathbf{R}_S)$ is given approximately by a space rigid shift of the 6D PES $V_{6D}(\mathbf{R}_A; \mathbf{R}_B)$,

$$V_{9D}(\mathbf{R}_A; \mathbf{R}_B, \mathbf{R}_S) = V_{6D}(\mathbf{R}_A - \mathbf{R}_S; \mathbf{R}_B - \mathbf{R}_S) + \frac{M_s}{2}(\omega_x^2 X_s^2 + \omega_y^2 Y_s^2 + \omega_z^2 Z_s^2) \quad (1.7)$$

Here, $\mathbf{R}_A$ and $\mathbf{R}_B$ are the coordinates of two H atoms, $\mathbf{R}_S$ is the rigid shift of the surface atom, ω_x , ω_y and ω_z are the surface oscillation frequencies, and M_s is the mass of the surface atom.

In the quantum dynamics employing the time-dependent wave packet study, the grid space in r degree of freedom is 0.085 a.u. (0.04 Å) which is much smaller than the one estimated from the uncertainty principle [74], 0.20 a.u.. The big grid needed to represent the potential energy surface and the wave function (Chapter 4 and Chapter 5) consumes a huge amount of memory, about 150 Gbytes. The total CPU time to do the convergence tests are also very large. The dynamics of the system itself is also slow to evolve (about 5000 fs) because of the trapping in the molecular adsorption well in front of the barrier. To avoid accumulating the propagation error in the split-operator method [103] (see Chapter 4), more accurate Lanczos method [104] can be tested, in which the evolution-operator can be approximated through a Taylor expansion to the p th order in the N -dimensional space ($p < N$),

$$\begin{aligned} \Psi(\mathbf{x}, t + \Delta t) &= e^{-i\hat{H}\Delta t} \cdot \Psi(\mathbf{x}, t) \\ &\approx \sum_{k=0}^{p-1} \frac{(-i\Delta t)^k}{k!} \mathbf{d}_k. \end{aligned} \quad (1.8)$$

Here, the $\mathbf{d}_k$ spans a so-called *Krylov space*,

$$\begin{aligned} \mathbf{d}_0 &= \Psi(\mathbf{x}, t) \\ \mathbf{d}_k &= \hat{H} \mathbf{d}_{k-1} \end{aligned} \quad (1.9)$$

Another Chebyshev method [105] (Chebyshev polynomial expansion of the evolution-operator acting on the initial wave packet) can also be tested.

The rate constants of H_2 dissociation on the 1/2 ML and 1 ML Ti/Al(100) surfaces obtained from the micro-canonical QCT reaction probabilities are always about 1 – 2

order of magnitudes larger than canonical rate constants obtained from TST and VTST in Chapter 5. We preliminarily assume that QCT results overestimate the rate constants due to the rovibrational energy leakage and the nonconservation of the quantization during the dynamics. However, in the trajectory studies of the gas phase bimolecular nucleophilic substitution (S_N2) with both a well and barrier, by Hase *et al.* [106, 107], show that the rate constants is inaccurately predicted by TST. The accuracy of the rate constants still needs to be established through comparison with experimental data.

1.5 References

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Chapter 2

Theoretical methods

2.1 The Born-Oppenheimer approximation

In the theoretical treatment of the dynamics of a chemical reaction, the motion of the electrons and the motion of the nuclei can be separated under the Born-Oppenheimer (BO) approximation [1]. Electrons will adjust their positions instantly whenever nuclei move, and the movement of the electrons depends on the particular positions of the nuclei.

For a molecule-surface process, the Hamiltonian describing the motion of nuclei and electrons can be given by

$$\hat{H} = T_e + T_N + V_{ee} + V_{eN} + V_{NN}, \quad (2.1)$$

where V_{ee} is the Coulomb repulsion potential between the electrons with charge e , V_{eN} is the Coulomb attraction potential between the electrons and the nuclei with charge Z_I , and V_{NN} is the Coulomb repulsion potential between the nuclei,

$$V_{ee} = \frac{1}{2} \sum_{ij(i \neq j)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.2)$$

$$V_{eN} = - \sum_{iI} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (2.3)$$

$$V_{NN} = \frac{1}{2} \sum_{IJ(I \neq J)} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad (2.4)$$

where $\mathbf{r}_i$ and $\mathbf{R}_I$ are the electronic and nuclear coordinates, respectively. The kinetic

energy operators T_e and T_N are given by,

$$T_e = - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 \quad (2.5)$$

$$T_N = - \sum_I \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2, \quad (2.6)$$

where m_e is the electron mass and M_I is the mass of the atom I. Because $m_e \ll M_I$, the term $T_N \ll T_e$ in Eq. 2.1 and T_N is negligible. Thus, the electronic Schrödinger equation can be solved with the nuclei fixed in a certain configuration,

$$\hat{H}\Psi(\mathbf{r}_i; \mathbf{R}_I) = E(\mathbf{R}_I)\Psi(\mathbf{r}_i; \mathbf{R}_I). \quad (2.7)$$

where $\hat{H} = T_e + V_{ee} + V_{eN} + V_{NN}$ under the BO approximation, and $\Psi(\mathbf{r}_i; \mathbf{R}_I)$ is the wave eigenfunction of the system fixed at a nuclear configuration $\mathbf{R}_I$. $E(\mathbf{R}_I)$ is the electronic eigenenergy of Eq. 2.7, which is called the *potential energy surface* (PES) and is subsequently used in solving the nuclear Schrödinger equation.

For a molecule-surface process, the BO approximation gives fairly accurate theoretical results in the systems of $\text{H}_2 + \text{Pt}(111)$ [2] and $\text{H}_2 + \text{Cu}(111)$ [3].

2.2 Brief density functional theory

2.2.1 From Hartree approximation to density functional theory

From Eq. 2.1 discussed above, the Hamiltonian of the system becomes ($\hbar = m_e = e = 1$, atomic units),

$$\hat{H} = - \sum_i \frac{1}{2} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{ij(i \neq j)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{2} \sum_{IJ(I \neq J)} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (2.8)$$

This system of electrons, ions and interactions can be solved by quantum mechanics with further simplifications.

In the implementation of quantum mechanics for this many-body problem, one of the approximations is to assume that the electrons do not interact with each other, but with the averaged density of the other electrons (mean field theory) [4]. The many-electron Schrödinger equation, Eq. 2.7 can be solved by N independent one-electron equations, this is known as the Hartree approximation. For N non-interacting electrons, the wave function is given by

$$\Psi^h(\mathbf{r}_i) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_N(\mathbf{r}_N). \quad (2.9)$$

Thus from Eq. 2.7 and Eq. 2.8, the total energy of the system is

$$\begin{aligned} E^h &= \langle \Psi^h | \hat{H} | \Psi^h \rangle \\ &= \sum_i \langle \phi_i | \frac{-1}{2} \nabla_{\mathbf{r}}^2 + V_{eN}(\mathbf{r}) | \phi_i \rangle + \frac{1}{2} \sum_{ij(i \neq j)} \langle \phi_i \phi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i \phi_j \rangle \end{aligned} \quad (2.10)$$

where the V_{NN} term in Eq. 2.4 is neglected, because it is simply a constant. A stationary state of the system can be obtained by taking the variation in the wave function subject to the constraint of normalization $\langle \phi_i | \phi_i \rangle = 1$, which gives the single-particle Hartree equations [4–6],

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V_{eN}(\mathbf{r}) + \frac{1}{2} \sum_{j \neq i} \langle \phi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_j \rangle \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (2.11)$$

where ϵ_i is the Lagrange multiplier. The last term on the left hand side of Eq. 2.11 is known as the Hartree potential $V_i^h(\mathbf{r})$ due to the presence of all other electrons (only Coulomb repulsion),

$$V_i^h(\mathbf{r}) = \frac{1}{2} \sum_{j \neq i} \langle \phi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_j \rangle. \quad (2.12)$$

Electrons are fermions. Due to the Pauli exclusion principle, no two particles can be described by the same one-particle function. The total wave function for the system must be an antisymmetric sum of all the products which can be obtained by interchanging electron labels. To incorporate the Pauli principle of electrons in the many-body wave function, the Hartree type wave function in Eq. 2.9 can be improved. For a 2-electron system, the wave function is given by

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) - \phi_2(\mathbf{r}_1) \phi_1(\mathbf{r}_2)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \end{vmatrix}. \end{aligned} \quad (2.13)$$

Here, $1/\sqrt{2}$ is the normalization factor. If we change the electron labels $1 \rightarrow 2$ and $2 \rightarrow 1$, we get

$$\begin{aligned} \Psi(\mathbf{r}_2, \mathbf{r}_1) &= \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_2) \phi_2(\mathbf{r}_1) - \phi_2(\mathbf{r}_2) \phi_1(\mathbf{r}_1)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \end{vmatrix}. \end{aligned} \quad (2.14)$$

The determinant representation of the total wave function is called a *Slater determinant*. From Eqs. 2.13 and 2.14, the antisymmetric property of the wave function can be verified to be,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1). \quad (2.15)$$

Following the same procedure for an N-electron system the total wave function (Slater determinant) is constructed by,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}. \quad (2.16)$$

As in the case of the Hartree approximation in Eq. 2.11, the single-particle Hartree-Fock equations can be obtained by employing the variational principle,

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V_{eN}(\mathbf{r}) + V_i^h(\mathbf{r}) \right] \phi_i(\mathbf{r}) - \sum_{j \neq i} \langle \phi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i \rangle \phi_j(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \quad (2.17)$$

Here there is an extra term compared to the Hartree equation, which is called the *exchange* term. The exchange term describes the anti-symmetric exchange between electrons. Now, we define the single-particle density and the total density as

$$\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2 \quad (2.18)$$

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}). \quad (2.19)$$

The single-particle Hartree-Fock equations in Eq. 2.17 then take the form

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V_{eN}(\mathbf{r}) + V_i^h(\mathbf{r}) + V_i^x(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (2.20)$$

where the exchange potential $V_i^x(\mathbf{r})$ is given by

$$V_i^x(\mathbf{r}) = \int \frac{\rho_i^x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (2.21)$$

and the single-particle exchange density $\rho_i^x(\mathbf{r}, \mathbf{r}')$ is constructed from,

$$\rho_i^x(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\phi_i(\mathbf{r}') \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}')}{\phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')}. \quad (2.22)$$

The Hartree potential takes the form,

$$V_i^h(\mathbf{r}) = \sum_{j \neq i} \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \int \frac{\rho(\mathbf{r}') - \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.23)$$

In the Thomas-Fermi approximation [7] of a homogeneous free electron gas system, the kinetic energy (the first term in Eq. 2.20 or Eq. 2.5) can also be expressed as a functional of density by

$$T_e^{TF} = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}. \quad (2.24)$$

Thus, the total energy is a functional of the electron density only already in the Thomas-Fermi theory.

2.2.2 Density functional theory

Instead of starting with a drastic approximation for the behaviour of the system (*i.e.* the Hartree or Hartree-Fock approximations to the wave function representations), one can develop the appropriate single-particle equations in an exact manner and then introduce approximations if necessary [4]. In the density functional theory (DFT), the many-body wave function $\Psi(\mathbf{r})$ is not dealt with directly, instead one considers the density of electrons $\rho(\mathbf{r})$. The basic ideas of DFT was developed by Hohenberg, Kohn and Sham [8, 9] and is also known as Hohenberg-Kohn-Sham theory.

The two Hohenberg-Kohn theorems [8] state that every observable of a stationary quantum mechanical system can be calculated, in principle exactly, from the electronic ground-state density alone, *i.e.*, every observable can be written as a functional of the ground-state density, and that the ground state density can be calculated, in principle exactly, using the variational method involving only the density. The theorems indicate that within the BO approximation, the nuclear positions determinate the ground state of the system of the electrons. The kinetic energy of the electrons (T_e) and the Coulomb repulsion potential between the electrons (V_{ee}) adjust themselves to a external potential U_{ext} (*i.e.*, the contribution from V_{eN} of the nuclei). Once the U_{ext} is in place, the electron density $\rho(\mathbf{r})$ simply adjusts itself to the lowest possible total energy of the system. The Hohenberg-Kohn theorems also pose a precise mapping from $\rho(\mathbf{r})$ to U_{ext} . The knowledge of $\rho(\mathbf{r})$ provides full information about the system.

The kinetic energy of electrons (T_e) can be calculated exactly from the wave function, rather than from the density in Eq. 2.24. This results in a ingenious method of marrying wave function and density approach by Kohn and Sham [9]. The total energy of the system can be reformed by

$$E[\rho] = T_e[\rho] + U_{ext}[\rho] + U_{ee}[\rho] \quad (2.25)$$

$$= T_0[\rho] + U_{ext}[\rho] + E_{ee}[\rho] + E_{xc}[\rho], \quad (2.26)$$

where U_{ee} is the all electron-electron interaction potential (including V_{ee}), $E_{ee}[\rho]$ is the Coulomb repulsion potential between the electrons in Eq. 2.2, and $T_e[\rho]$ and $T_0[\rho]$ are the kinetic energy in an interacting and non-interacting electron system, respectively. The new functional term $E_{xc}[\rho]$, is called the *exchange-correlation energy* defined by

$$E_{xc}[\rho] = T_e[\rho] - T_0[\rho] + U_{ee}[\rho] - E_{ee}[\rho]. \quad (2.27)$$

It includes all the energy contributions which are not accounted for in $T_0[\rho]$ and $E_{ee}[\rho]$. In fact, if we know E_{xc} , the total energy in Eq. 2.25 can be calculated exactly. By applying the variational principle (as in the previous Hartree and Hartree-Fock methods), the non-interacting single particle Kohn-Sham equation can be obtained,

$$\left[-\frac{1}{2}\nabla_i^2 + V_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r}), \quad (2.28)$$

where $\phi_i^{KS}(\mathbf{r})$ are called the *Kohn-Sham orbitals*, which can be used to compute the total density

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{KS}(\mathbf{r})|^2, \quad (2.29)$$

and $V_{eff}(\mathbf{r})$ is an effective potential defined as,

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{xc}(\mathbf{r}), \quad (2.30)$$

where the exchange-correlation potential $V_{xc}(\mathbf{r})$ is found from the variation of the exchange-correlation energy $V_{xc}(\mathbf{r}) = \delta E_{xc}[\rho(\mathbf{r})]/\delta \rho(\mathbf{r})$. In the local density approximation (LDA), the functional E_{xc}^{LDA} is given by

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = E_x^{LDA}[\rho(\mathbf{r})] + E_c^{LDA}[\rho(\mathbf{r})], \quad (2.31)$$

where $E_x^{LDA}[\rho(\mathbf{r})]$ is the exchange energy approximated by [10]

$$E_x^{LDA}[\rho(\mathbf{r})] = \int \epsilon_x[\rho(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} \quad (2.32)$$

$$= -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \rho(\mathbf{r})^{1/3}, \quad (2.33)$$

and $\epsilon_x[\rho(\mathbf{r})]$ is the exchange energy per electron in an electron gas with density $\rho(\mathbf{r})$. The correlation energy is expressed as,

$$E_c^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\epsilon_c[\rho(\mathbf{r})]d\mathbf{r} \quad (2.34)$$

where $\epsilon_c[\rho(\mathbf{r})]$ is the correlation energy per electron in an electron gas with density $\rho(\mathbf{r})$. The LDA is known to overbind most molecular bonds. It gives a too low barrier to dissociation for the $\text{H}_2 + \text{Cu}(100)$ [11, 12], $\text{H}_2 + \text{Cu}(111)$ [13], and $\text{H}_2 + \text{Pd}(111)$ [14] systems.

A notable improvement over the LDA is the generalized gradient approximation (GGA) obtained by expanding $E_{xc}[\rho]$ to the first order to consider both the density and its gradient,

$$E_{xc}^{GGA}[\rho, \nabla \rho] = \int f(\rho, \nabla \rho)d\mathbf{r}. \quad (2.35)$$

In molecule-surface reactions, the most widely used GGAs are the PW91 (Perdew and Wang in 1991) [15] and RPBE (revised Perdew-Burke-Ernzerhof) [16] functionals.

2.2.3 Plane wave DFT

In the earlier 1930's, Stutt and Block [17] investigated the properties of the Schrödinger equation for an electron in a periodic potential, and the existence of energy bands was discovered. For a particle in a three-dimensional periodic potential $V(\mathbf{r})$ with a period $\mathbf{l}$ such that,

$$V(\mathbf{r} + n\mathbf{l}) = V(\mathbf{r}) \quad (2.36)$$

for all integral values of n , the Schrödinger equation

$$\frac{d^2\psi}{dr^2} + V(\mathbf{r}) = 0 \quad (2.37)$$

has a periodic solution,

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \quad (2.38)$$

where $f(x)$ is periodic with $f(\mathbf{r} + n\mathbf{l}) = f(\mathbf{r})$, and $\mathbf{k}$ is a real number that appears in the wave function. The $\mathbf{k}$ value ensures the periodicity of the wave function. In other words, the meaning of $\mathbf{k}$ relates to the degree of freedom $\mathbf{r}$ where the particle can have a continuous momentum.

The Bloch's theorem states that in a periodic solid each electronic wave function can be written as a product of a cell-periodic part ($e^{i\mathbf{k}\cdot\mathbf{r}}$) and a wave-like part [$f(\mathbf{r})$] as in Eq. 2.38 [18]. The wave-like part of the wave function can be expanded using a basis set consisting of discrete set of plane waves

$$f(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (2.39)$$

where $C_{\mathbf{G}}$ are the expansion coefficients and $\mathbf{G}$ is a reciprocal lattice vector defined by

$$\mathbf{G} \cdot \mathbf{l} = 2\pi n. \quad (2.40)$$

Therefore, a combination of Eq. 2.38 and Eq. 2.39 gives the electronic wave function as a linear combination of plane waves for DFT as,

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} C_{i,\mathbf{k}+\mathbf{G}} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (2.41)$$

where Ω is the volume of the unit cell and $1/\sqrt{\Omega}$ is the normalization constant of the wave function. The plane wave basis set is not only periodic but also orthogonal and complete, which makes it convenient to calculate the expansion coefficients. An example of orthogonality is given by

$$\langle \psi_{\mathbf{G}'}(\mathbf{r}) | \psi_{\mathbf{G}}(\mathbf{r}) \rangle = \delta_{\mathbf{G}'\mathbf{G}}. \quad (2.42)$$

where $\psi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}' \cdot \mathbf{r}}$.

By substituting the plane waves of Eq. 2.41 into the single particle Kohn-sham equations of Eq. 2.28, multiplication from left by $\frac{1}{\sqrt{\Omega}} e^{-i(\mathbf{k}+\mathbf{G}') \cdot \mathbf{r}}$ and integration over $\mathbf{r}$, the plane wave Kohn-Sham equation can be obtained [18],

$$\sum_{\mathbf{G}} \left[\frac{1}{2} |\mathbf{k} + \mathbf{G}'|^2 \delta_{\mathbf{G}'\mathbf{G}} + V^h(\mathbf{G}' - \mathbf{G}) + V_{xc}(\mathbf{G}' - \mathbf{G}) + V_{eN}(\mathbf{G}' - \mathbf{G}) \right] C_{i,\mathbf{k}+\mathbf{G}} = \epsilon_i C_{i,\mathbf{k}+\mathbf{G}'} \quad (2.43)$$

Here $V^h(\mathbf{G}' - \mathbf{G})$ is the Hartree potential in Eq. 2.23, $V_{xc}(\mathbf{G}' - \mathbf{G})$ is the exchange correlation potential in Eq. 2.30, and $V_{eN}(\mathbf{G}' - \mathbf{G})$ is the electron-nuclei ionic potential in Eq. 2.3. The Eq. 2.43 can be solved by successive improvement of a trial wave function through the procedure of a self-consistent field approach [18].

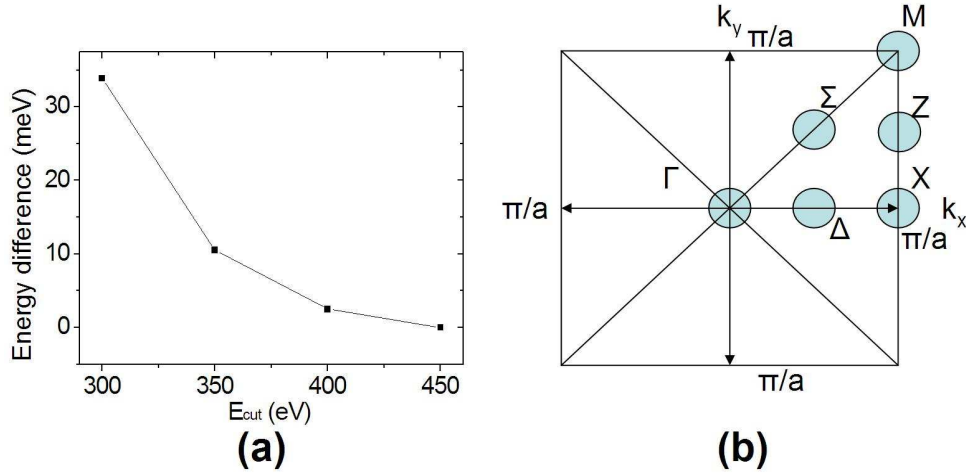


Figure 2.1: (a) Cutoff energy E_{cut} convergence test for a four-layer Ti/Al(100) slab with a $\mathbf{k}$ -point sampling by $(8 \times 8 \times 1)$ for (k_x, k_y, k_z) , respectively. (b) $\mathbf{k}$ -point sampling in the Brillouin zone of a slab model same as in (a), but with a density of $\mathbf{k}$ -points of $(4 \times 4 \times 1)$. The light blue circles indicate the positions of the $\mathbf{k}$ -points in the kinetic space k_x and k_y .

A discrete set of plane waves is required to expand the electronic wave functions at each $\mathbf{k}$ -point in Eq. 2.41. To reduce the number of plane waves, the effect of high kinetic energy core electrons can be described by pseudopotentials. Then the kinetic energy can be truncated according to the plane wave cutoff energy E_{cut} ,

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}_C|^2 \leq E_{cut} \quad (2.44)$$

where $\mathbf{G}_C$ is the cutoff value of the kinetic energy. The appropriate value of E_{cut} for a given system should be established by a set of convergence tests. An example of such a

plane wave cutoff energy test shows that $E_{cut} = 400$ eV gives rather well converged results for the given system, with an error of only about 2.50 meV, see Fig. 2.1 (a).

Finally, the number of $\mathbf{k}$ -points needed is in principle infinite for an infinite crystal. But wave functions at $\mathbf{k}$ -points that are very close together will be almost identical. Hence it is possible to represent the electronic wave functions over a region by a single $\mathbf{k}$ -point. In this case, only a finite number of $\mathbf{k}$ -points is required to calculate the electronic potential and hence determine the total energy of the solid. In Fig. 2.1 (b), an example is given for an irreducible $\mathbf{k}$ -point sampling in the Brillouin zone of a $c(2 \times 2)$ -Ti/Al(100) surface according to the C_{4v} symmetry of the surface. $\Gamma(0, 0)$ and $M(\pi/a, \pi/a)$ have the full C_{4v} symmetry. Other special points X, Δ, Σ and Z either have the symmetry of rotation (C_2 symmetry) or have the symmetry of reflection (σ). From Fig. 2.1, we can see that the high symmetry points are covered by the sampling of $(4N \times 4N \times 1)$ for (k_x, k_y, k_z) , respectively, where N is a positive integer. An odd number $\mathbf{k}$ -point sampling, e.g. $(5 \times 5 \times 1)$ can not cover the high symmetry points except the Γ point.

2.2.4 Two-center projected density of states

To understand the mechanism of H_2 dissociation, the two-center projected density of states (PDOS) may be calculated at energies ε of the localized orbital ϕ_a , as

$$n_a(\varepsilon) = \sum_i \sum_k |\langle \phi_a | \psi_{ik} \rangle|^2 \delta(\varepsilon - \varepsilon_{ik}), \quad (2.45)$$

where i runs over all electronic bands, and k labels the $\mathbf{k}$ -points used for sampling the Brillouin zone. The ψ_{ik} are the periodic Kohn-Sham wave functions discussed in Eq. 2.41 and the ε_{ik} are the corresponding eigenvalues. The Fermi level is taken as the energy zero. The δ function is taken as a Gaussian expanded with a width of 0.20 eV. The ϕ_a can be chosen as the H_2 molecular bonding (σ_g) and antibonding (σ_u) orbitals, which are constructed as the normalized linear combinations of hydrogen s orbitals, ϕ_s^H , centered at the positions of the two hydrogen atoms $\mathbf{R}_1$ and $\mathbf{R}_2$:

$$\phi_{\sigma_g}(\mathbf{r}) = c_1 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) + \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (2.46)$$

$$\phi_{\sigma_u}(\mathbf{r}) = c_2 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) - \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (2.47)$$

where $c_1 = 1/\sqrt{2(1+S)}$, $c_2 = 1/\sqrt{2(1-S)}$ are the normalization coefficients, and S is the overlap term $S = \int \phi_s^{H*}(\mathbf{r} - \mathbf{R}_1) \phi_s^H(\mathbf{r} - \mathbf{R}_2) d\tau$, which is analytically calculated by [19, 20],

$$S = \left\{ 1 + \frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} + \frac{1}{3} \left(\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} \right)^2 \right\} e^{-|\mathbf{R}_1 - \mathbf{R}_2|/a_0}, \quad (2.48)$$

where a_0 is the Bohr radius.

2.3 Quasi-Newton optimization for stationary points

Under the BO approximation, a given H_2 -surface system can be solved by solving the plane wave Kohn-Sham equation in Eq. 2.43, which provides the energy (eigenvalues) and optimized electronic structure (wave function) of the system, in what is known as a single-point calculation. To find out the stationary points (*i.e.*, the equilibrium atom-atom distance, position of molecular adsorption wells) and the transition state, geometry optimization needs to be performed. One of the most common methods, the quasi-Newton optimization is used in this thesis.

In the steepest descent (SD) method, only the force components [or negative direction gradients $\mathbf{g}_i(\mathbf{X}_i)$] are considered for obtaining the displacement vector, $\mathbf{X}_{i+1} = \mathbf{X}_i - \lambda_i \mathbf{g}_i(\mathbf{X}_i)$, where $\mathbf{X}_i$ is the sequence of the points needed to find a stationary point, and λ_i is a step size,

$$\partial f(\mathbf{X}_i - \lambda_i \mathbf{g}_i(\mathbf{X}_i)) / \partial \lambda_i = 0. \quad (2.49)$$

The SD method is easy to implement but too slow in finding a stationary point. In the Newton method second order derivatives are employed to speed up direction searches. Given the second order Taylor expansion

$$f(\mathbf{X}_{i+1}) = f(\mathbf{X}_i) + \mathbf{g}_i \Delta \mathbf{X}_i + \frac{1}{2} \Delta \mathbf{X}_i^T \mathbf{H}_i \Delta \mathbf{X}_i, \quad (2.50)$$

where $\mathbf{H}_i$ is the Hessian matrix at the i th step, with the gradient of $f(\mathbf{X}_{i+1})$ given by

$$\mathbf{g}_{i+1} = \mathbf{g}_i + \mathbf{H}_i \Delta \mathbf{X}_i, \quad (2.51)$$

where $\mathbf{g}_{i+1} = \nabla f(\mathbf{X}_{i+1})$, a stationary point can be found when $\mathbf{g}_i + \mathbf{H}_i \Delta \mathbf{X}_i = 0$. Thus the iterative scheme is given by [21],

$$\mathbf{X}_{i+1} = \mathbf{X}_i - \mathbf{H}_i^{-1} \mathbf{g}_i. \quad (2.52)$$

To illustrate the Newton process, an example is given to find the stationary point in a 2D function $f(x, y) = x - y + 2x^2 + 2xy + y^2$ from Ref. [21]. Starting from an initial point $X_1 = (0, 0)$ [the known stationary point is $(-1, 1.5)$, see Fig. 2.2], the Hessian matrix can be calculated by

$$\mathbf{H}_1 = \begin{bmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} \end{bmatrix}_{\mathbf{X}_1} = \begin{bmatrix} 4 & 2 \\ 2 & 2 \end{bmatrix}, \quad (2.53)$$

and the gradient vector $\mathbf{g}_1$ is given by

$$\mathbf{g}_1 = \begin{bmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \end{bmatrix}_{\mathbf{X}_1} = \begin{bmatrix} 1 \\ -1 \end{bmatrix}. \quad (2.54)$$

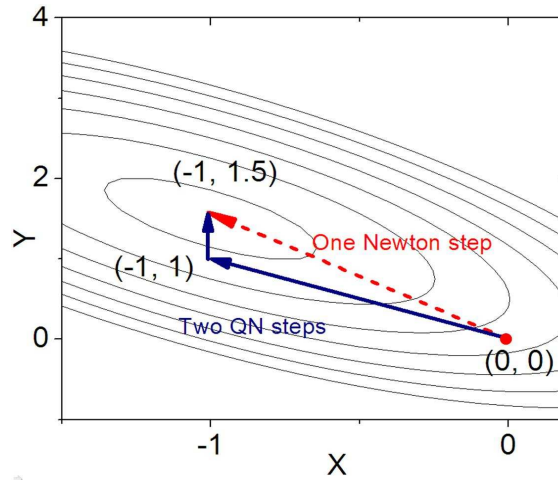


Figure 2.2: Minimization of a quadratic function $f(x, y) = x - y + 2x^2 + 2xy + y^2$ by the Newton and quasi-Newton methods. The Newton method only needs one step (dotted line) to find the stationary point, while the QN method needs two steps (solid lines). The function was chosen by Rao in Ref. [21].

From Eq. 2.52, the position of the second point can be calculated by

$$\mathbf{X}_2 = \mathbf{X}_1 - \mathbf{H}_1^{-1} \mathbf{g}_1 = \begin{bmatrix} -1 \\ 1.5 \end{bmatrix}. \quad (2.55)$$

The convergence criterium has been met already because $\mathbf{g}_2(\mathbf{X}_2) = (0, 0)^T$.

In the Quasi-Newton (QN) method, the $\mathbf{H}$ matrix is calculated approximately from the gradient differences. Using Eq. 2.51, the $(i + 1)$ th step expression gives,

$$\mathbf{H}_{i+1}(\mathbf{X}_{i+2} - \mathbf{X}_{i+1}) = \mathbf{g}_{i+2} - \mathbf{g}_{i+1}. \quad (2.56)$$

If $\mathbf{X}_{i+2}$ is the stationary point, then $\mathbf{g}_{i+2} = 0$. Thus it yields the secant equation [21, 22] to estimate the $\mathbf{H}$ matrix,

$$\mathbf{H}_{i+1} \Delta \mathbf{X}_{i+1} = -\mathbf{g}_{i+1}. \quad (2.57)$$

The assumption of $\mathbf{X}_{i+2}$ being a stationary point is in general obviously not true. The Eq. 2.57 is then just used as a direction for the next step. The new point $\mathbf{X}_{i+2}$ is modified by a minimization of the step length λ_{i+1} (see Eq. 2.49) along the direction of $-\mathbf{H}_{i+1}^{-1} \mathbf{g}_{i+1}$,

$$\mathbf{X}_{i+2} = \mathbf{X}_{i+1} - \lambda_{i+1} \mathbf{H}_{i+1}^{-1} \mathbf{g}_{i+1}. \quad (2.58)$$

In the Davidon-Fletcher-Powell (DFP) method [21], the QN is implemented as:

(1) Start from a guessed initial point $\mathbf{X}_1$ and a $n \times n$ positive definite symmetric matrix

$\mathbf{H}_1$, usually an identity matrix $\mathbf{I}$.

(2) Compute the $\mathbf{g}_i$ and $-\mathbf{H}_i^{-1}\mathbf{g}_i$ in Eq. 2.58.

(3) Find the optimal λ_{i+1} from Eq. 2.49 and calculate $\mathbf{X}_{i+1}$ in Eq. 2.58.

(4) Check the convergence of the new point $\mathbf{X}_{i+1}$ by calculating $\mathbf{g}_{i+1}$. If $\mathbf{g}_{i+1} = 0$, $\mathbf{X}_{i+1}$ is a stationary point. Otherwise go to (5).

(5) Update $\mathbf{H}$ matrix,

$$\mathbf{H}_{i+1} = \mathbf{H}_i + \mathbf{M}_i + \mathbf{N}_i \quad (2.59)$$

$$\mathbf{M}_i = \lambda_i \frac{\Delta \mathbf{X}_i \Delta \mathbf{X}_i^T}{\Delta \mathbf{X}_i^T \mathbf{Q}_i} \quad (2.60)$$

$$\mathbf{N}_i = -\frac{(\mathbf{H}_i \mathbf{Q}_i)(\mathbf{H}_i \mathbf{Q}_i)^T}{\mathbf{Q}_i^T \mathbf{H}_i \mathbf{Q}_i} \quad (2.61)$$

$$\mathbf{Q}_i = \mathbf{g}_{i+1} - \mathbf{g}_i \quad (2.62)$$

and go to step (2) for an iteration to $i + 1$.

Now, we can also use this QN procedure to find the stationary point for the 2D function $f(x, y) = x - y + 2x^2 + 2xy + y^2$, starting from $\mathbf{X}_1 = (0, 0)^T$ (also see Fig. 2.2):

Step 1

$\mathbf{g}_1 = (1, -1)^T$ can be calculated as in the Newton method, $\mathbf{H}_1 = \mathbf{I}_{2 \times 2}$, and $-\mathbf{H}_1^{-1}\mathbf{g}_1 = (-1, 1)$. The optimal λ_{i+1} can be determined from Eq. 2.49

$$\frac{\partial f(\mathbf{X}_1 - \lambda_1 \mathbf{H}_1^{-1} \mathbf{g}_1)}{\partial \lambda_1} = \frac{\partial f(-\lambda_1, \lambda_1)}{\partial \lambda_1} = 2\lambda_1 - 2 = 0. \quad (2.63)$$

Thus $\lambda_1 = 1$ and $\mathbf{X}_2 = \mathbf{X}_1 - \lambda_1 \mathbf{H}_1^{-1} \mathbf{g}_1 = (-1, 1)^T$, which yields $\mathbf{g}_2 = (-1, -1)$, thus the convergence has not yet been achieved.

Step 2

The vector $\mathbf{Q}_1$ in Eq. 2.62 can be calculated by $\mathbf{Q}_1 = \mathbf{g}_2 - \mathbf{g}_1 = (-2, 0)^T$. From Eq. 2.60 and Eq. 2.61, the matrices $\mathbf{M}_1$ and $\mathbf{N}_1$ can be obtained, $\mathbf{M}_1 = \frac{1}{2} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$ and $\mathbf{N}_1 = \begin{bmatrix} -1 & 0 \\ 0 & 0 \end{bmatrix}$, respectively. The new Hessian $\mathbf{H}_2 = \mathbf{H}_1 + \mathbf{M}_1 + \mathbf{N}_1 = \frac{1}{2} \begin{bmatrix} 1 & -1 \\ -1 & 3 \end{bmatrix}$. The new optimal λ_2 can be obtained as $\lambda_2 = 0.5$, $\mathbf{X}_3 = \mathbf{X}_2 - \lambda_2 \mathbf{H}_2^{-1} \mathbf{g}_2 = (-1, 1.5)^T$, and the gradient vector $\mathbf{g}_3 = (0, 0)^T$ indicates that $\mathbf{X}_3$ is a stationary point as found by the Newton method (see Fig. 2.2).

2.4 Barrier search methods

Once the barrier position and barrier height and the potential minima of a system are obtained, the basic properties of the dynamics can be estimated, *i.e.* the reaction is an

endothermic or exothermic process, activated or non-activated process. According to Polanyi's rule [23], developed to predict the role of vibrational and collisional energy in driving reactions overcoming a barrier for simple three body exchange reactions $A + BC \rightarrow AB + C$, vibrational excitation should be efficient at enhancing a reaction when the system has a late barrier, and the reverse is true when the system has an early barrier.

In this thesis, H_2 dissociation barrier heights are obtained using the adaptive nudged elastic band (ANEb) method [24, 25]. In our example, both initial and final configurations have the same center of mass (COM) X and Y coordinates of the H_2 molecule. The initial H_2 gas phase configurations, H_2 is 4.0 Å above the surface, and parallel to the surface with a bond length of 0.755 Å. Final dissociated H-H configurations describe the relaxed atomic chemisorption minima on the slab. To obtain reaction paths, three images

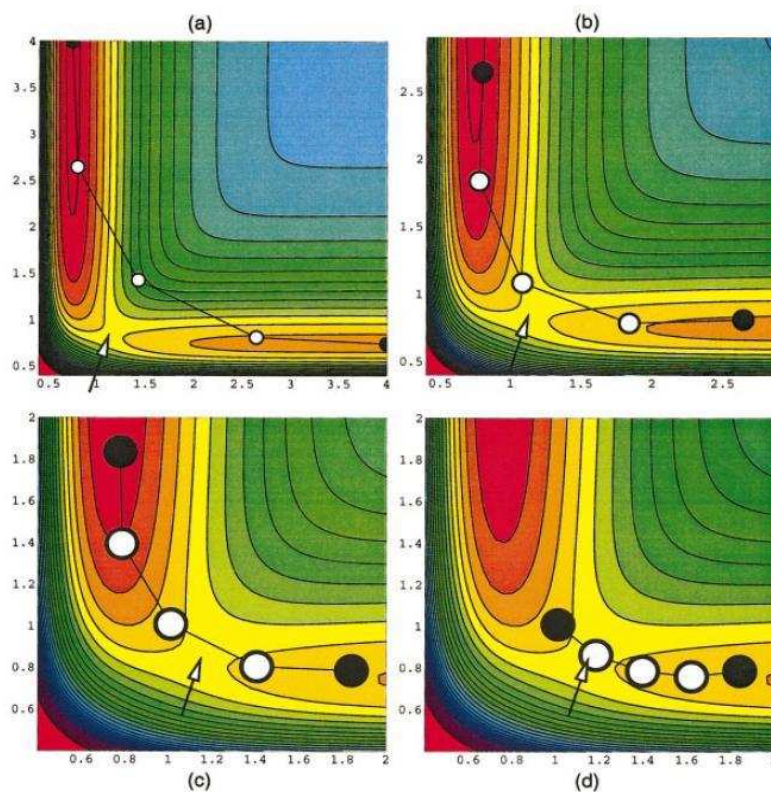


Figure 2.3: Successive steps of the adaptive search of the saddle point in a simple model potential. The closed circles stand for the fixed end-point images at each iteration step, and the open circles show the final location of the moving images. The arrow indicates the exact location of the saddle point [25].

are linearly interpolated and equally spaced between the initial and final configurations. Artificial spring forces are added between the adjacent images, see Fig.2.3. We have to avoid that the images cut corners of the PES or slide down from the saddle point. One

way is to use the quasi-Newton minimization method to relax the component of the imaginary spring forces $\mathbf{F}_{\parallel}^{imag}$ only tangent to the reaction path, and the component of the real Coulomb forces $\mathbf{F}_{\perp}^{real}$ orthogonal to the reaction path. Then the total force on an image i is given by

$$\mathbf{F}_i = \mathbf{F}_{i\parallel}^{imag} + \mathbf{F}_{i\perp}^{real}. \quad (2.64)$$

Here, $\mathbf{F}_i$ can be converged to be as small as necessary for an accurate determination of the barrier location and height, *i.e.*, within 0.05 eV/Å. The next step is to discard the image with the highest potential energy value, and make the second interpolation between the two images closest to the discarded image. The example in Fig.2.3 shows a four step ANEB calculations that finds the converged barrier position.

It can sometimes be hard for the NEB method to obtain an accurate saddle point position for a system with many degrees of freedom (see the $\text{H}_2 + \text{Ti}/\text{Al}(100)$ systems in Chapter 4 and Chapter 5), because only the first-order derivatives are considered in relaxation. Another barrier search method, the climbing images nudged elastic band (CINEB) calculation [26] can converge to the saddle point at the same rate as a single NEB calculation. In the CINEB method, the highest energy image is at a certain stage freed from the spring forces and the potential inverted for that state while using only the projection along the path of the potential forces. This allows the highest energy image to search for the peak of potential, thereby obtaining the peak of minimum energy path (MEP), which is defined as the saddle point [25, 26].

2.5 Potential energy surface building

In order to calculate the precise reaction probability at a certain collision energy, a global potential energy surface is needed. In addition, an analysis of the PES topology is useful for the analysis of the reaction mechanism of a system.

For a simple system, the most commonly used analytical functions have these forms:
(1) Morse potential

$$V(r) = D_e[1 - e^{-2\alpha(r-r_e)^2}], \quad (2.65)$$

where r_e is the equilibrium internuclear distance and D_e is the dissociation energy.

(2) Taylor series expansion

$$V(r) = V(r_e) + \frac{1}{2!} \left(\frac{d^2V}{dr^2} \right) r_e (r - r_e)^2 + \frac{1}{3!} \left(\frac{d^3V}{dr^3} \right) r_e (r - r_e)^3 + \dots, \quad (2.66)$$

(3) N-body expansion [27]

$$V_{abc\dots n} = \sum V_a^{(1)} + \sum V_{ab}^{(2)} R_{ab} + \sum V_{abc}^{(3)} R_{ab'} R_{bc'} R_{ca'} + \dots, \quad (2.67)$$

where $\sum V_a^{(1)}$ is the sum of all one-body terms, $V_{ab}^{(2)} R_{ab}$ is the two-body term that is a function of the separation of two atoms, and $V_{abc}^{(3)}$ is a three-body term that depends on the dimension of the abc triangle.

(4) Least square fitting (LSF)

For a given m points, *e.g.* a one-dimensional data set of $(x, y(x))$ can be fitted to a function order of n ($n \leq m$), $y(x) = c_0 + c_1x + c_2x^2 + \dots + c_nx^n = \mathbf{C} \cdot \mathbf{B}$, where $\mathbf{C}$ is the unknown coefficients and $\mathbf{B}$ is the basis functions $(1, x, x^2, \dots, x^n)$. The coefficients can be calculated from the minimization of the square errors from

$$\frac{\partial \sum_{i=1}^m (\mathbf{C} \cdot \mathbf{B}_i - y_i)^2}{\partial \mathbf{C}} = 0, \quad (2.68)$$

which yields the coefficients from the solution of

$$\left(\sum_{i=1}^m \mathbf{B}_i \mathbf{B}_i^T \right) \mathbf{C} = \sum_{i=1}^m y_i \mathbf{B}_i. \quad (2.69)$$

(5) Fourier expansion

The fitting functions in the LSF can be chosen as a trigonometric polynomial. Especially, if the m even points ($m = 2n$) are equally spaced on an interval of length 2π , $y(x)$ can be given as,

$$y(x) = \frac{a_0}{2} + a_1 \cos x + a_2 \cos 2x + \dots + \frac{a_n}{2} \cos nx + b_1 \sin x + b_2 \sin 2x + \dots + b_n \sin nx. \quad (2.70)$$

Since the basis functions are orthogonal, the coefficients a_i , b_i can be easily obtained through the diagonal matrix in Eq. 2.69,

$$a_i = \frac{2}{m} \sum_{k=0}^{m-1} y_k \cos(i x_k), \quad b_i = \frac{2}{m} \sum_{k=0}^{m-1} y_k \sin(i x_k). \quad (2.71)$$

For a high dimensional H_2 -surface system, a statistical ‘‘Grow’’ method and an analytical PES construction by the corrugation reducing procedure have been implemented in this thesis, which we discuss next.

2.5.1 The “grow” method

The modified Shepard (MS) interpolation method [28–31] by Collins and coworkers, initially developed for gas phase reactions, has been adapted for studying reactions of molecule-surface dissociative chemisorption [32]. The procedures of the application of the MS interpolation is informally known as the “grow” method [28–31, 33], in which the data points can be calculated by DFT. The location of these data points are in the dynamically interesting regions, *i.e.*, the most frequently visited regions by quasi-classical trajectories. It is found that the MS interpolation method is efficient and accurate enough compared with the corrugation reduced procedure (CRP) in the previous works by Busnengo and coworkers [34–36].

For higher dimensionality, MS interpolation is an efficient method to get accurate descriptions of the potential energy surface. Successful applications of MS method to dissociative chemisorption of molecules on metal surfaces have been performed in the previous studies [32, 33, 37, 38].

The PES is constructed by using inverse interatomic distances $Q_i = 1/R_i$, which give a better mathematical behavior than the interatomic distances R_i when two atoms come close to each other (the singularities at $R_i \rightarrow 0$ are transformed away to $Q_i \rightarrow \infty$). For a system with N atoms, the number of interatomic distances is given by $N(N-1)/2$. Thus, in the system of $H_2 + Ti/Al(100)$, $N = 5$ atoms are required with two hydrogen and three frozen surface atoms to represent the problem, in which two Ti atoms and one Al atoms form an isosceles right triangle. A configuration in the system is described using a vector of inverse inter-atomic distances, $\mathbf{Q} = \{Q_1, Q_2, \dots, Q_{N(N-1)/2}\}$. For any configuration of the system $\mathbf{Q}$, a vector of $3N - 6$ independent coordinates, $\xi(\mathbf{Q})$, can be defined in terms of the inverse interatomic distances, via a singular value decomposition [29, 31, 32]:

$$\xi_n = \sum_{k=1}^{N(N-1)/2} U_{nk} Q_k \quad (n = 1, \dots, 3N - 6). \quad (2.72)$$

According to the MS interpolation method, the potential at a given configuration $\mathbf{Q}$, in the vicinity of $\mathbf{Q}(i)$, is given by a second-order Taylor expansion $T_i(\mathbf{Q})$:

$$\begin{aligned} T_i(\mathbf{Q}) = & V[\mathbf{Q}(i)] + \sum_{k=1}^{3N-6} [\xi_k - \xi_k(i)] \frac{\partial V}{\partial \xi_k} \Big|_{\mathbf{Q}=\mathbf{Q}(i)} \\ & + \frac{1}{2} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} [\xi_k - \xi_k(i)] [\xi_j - \xi_j(i)] \frac{\partial^2 V}{\partial \xi_k \partial \xi_j} \Big|_{\mathbf{Q}=\mathbf{Q}(i)}. \end{aligned} \quad (2.73)$$

The value of the potential energy at data point $\mathbf{Q}(i)$, $V[\mathbf{Q}(i)]$, and the gradients with respect to ξ at this point are calculated analytically with DFT. The second derivatives of

the potential are calculated using numerical forward finite differences of the gradients, displacing the H atoms by 0.01 Å.

The MS interpolation gives the potential energy at any configuration $\mathbf{Q}$ as a weighted average of the Taylor expansion terms $T_i (i = 1, \dots, N_{data})$ calculated from each of the N_{data} data points presented in the PES data set and all their symmetry equivalents:

$$V(\mathbf{Q}) = \sum_{g \in G} \sum_{i=1}^{N_{data}} w_{g \circ i}(\mathbf{Q}) T_{g \circ i}(\mathbf{Q}). \quad (2.74)$$

In Eq. 2.74, G is the symmetry subgroup of the system and $g \circ i$ denotes the transformation of the i th data point by the group element g . The symmetry of the system is taken into account by summing over the data points in the PES data set and the symmetry equivalent points. The nuclear permutation subgroup, C_{2v} is used for the system of Ti/Al(100) (the isosceles right triangle with two Ti atoms and one Al atom as mentioned above), although the full symmetry should be C_{4v} . The absence of the full C_{4v} surface symmetry is accepted because the number of interatomic distances will increase dramatically with introducing more surface atoms into the representation of PES by the Taylor expansion in Eq. 2.73, as would be required.

The normalized weight function $w_{g \circ i}(\mathbf{Q})$ for a given configuration $\mathbf{Q}$ depends on how close it is to another configuration $\mathbf{Q}(i)$ in the configuration space, and is defined by

$$w_{g \circ i}(\mathbf{Q}) = \frac{v_i(\mathbf{Q})}{\sum_{g \in G} \sum_{k=1}^{N_{data}} v_{g \circ k}(\mathbf{Q})}. \quad (2.75)$$

The unnormalized weight function, $v_i(\mathbf{Q})$, can have two forms. When there are few points (less than 500) in the data set, a simple one-part weight function form for $v_i(\mathbf{Q})$ is used

$$v_i(\mathbf{Q}) = \frac{1}{\|\mathbf{Q} - \mathbf{Q}(i)\|^{2p}}, \quad (2.76)$$

where we take $2p > 3N - 3$ to ensure that data points $\mathbf{Q}(i)$ far from the configuration $\mathbf{Q}$ make a negligible contribution to the interpolated energy. When there are a sufficient number of data points, a more accurate form of the unnormalized two-part weight function is employed

$$v_i(\mathbf{Q}) = \left\{ \left[\sum_{n=1}^{N(N-1)/2} \left(\frac{Q_n - Q_n(i)}{rad_n(i)} \right)^2 \right]^q + \left[\sum_{n=1}^{N(N-1)/2} \left(\frac{Q_n - Q_n(i)}{rad_n(i)} \right)^2 \right]^p \right\}^{-1}, \quad (2.77)$$

where $p = 12$ and $q = 2$. The *confidence radius* $rad_n(i)$ is defined by Bayesian analysis [31] of an energy error tolerance (0.54 meV used in this paper) and a restricted set C of nearest neighbouring data points ($C = 40$ points in the present work). The trick

of the two-part weight function ensures that the Taylor expansion does not spuriously introduce sharp gradients in the PES. For example, the Taylor expansion is not just a function of distance, it is also a function of direction. Distorting a data point geometry in one direction might correspond to compressing an already short bond, so the quadratic Taylor expansion alone in Eq. 2.73 is unlikely to be accurate over a large distortion of the molecule. Conversely, distorting a data point geometry in another direction might correspond to a relative rotation of two distant molecule fragments which is accurately described by the Taylor expansion [31]. Hence, the confidence radius in Eq. 2.77 confines the Taylor expansion to its safe range.

An advantage of the MS interpolation method over other interpolation methods is that it does not require a regular and uniform grid of data points. Instead, the sampling of data points can be non-uniformly distributed over the configuration space. Therefore, only the dynamically relevant regions of the PES will contribute significantly by adding points to the data set. These dynamically relevant regions are found by performing quasi-classical trajectory (QCT) calculations (details discussed in the next subsection). The new data points to be added to the PES data set are selected according to the *h-weight* criterium, by which the new points are added in the region most frequently visited by the trajectories. In this *h-weight* criterium, different configurations N_{traj} sampled by the trajectories are stored every 50 time steps [$\Delta t = 1.033 \times 10^{-2}$ femtosecond (fs)]. The quality of $h(k)$ is calculated for each of these configurations by,

$$h(k) = \frac{\sum_{m=1, m \neq k}^{N_{traj}} v_m[\mathbf{Q}(k)]}{\sum_{i=1}^{N_{data}} v_i[\mathbf{Q}(k)]}, \quad (2.78)$$

in which the sum over m is over all points recorded in the classical trajectories, and v_m is the unnormalized weight function in Eq. 2.77, which is based on the difference between the recorded geometry $\mathbf{Q}(k)$ and all the geometries of N_{traj} points in the numerator term. The integer i sums over the points in the data set, N_{data} in the denominator term. The value of $h(k)$ is large when $\mathbf{Q}(k)$ is both near other points visited by the trajectories and far away from the points in the data set.

In the variance criterium [31], it is assumed that a new added point should be in the region where the interpolation by the weighted Taylor expansions is the most inaccurate, according to a weighted mean square deviation criterium,

$$\sigma^2(k) = \sum_{i=1}^{N_{data}} w_i[\mathbf{Q}(k)] \{T_i[\mathbf{Q}(k)] - V[\mathbf{Q}(k)]\}^2. \quad (2.79)$$

Here, $V[\mathbf{Q}(k)]$ is the interpolated energy in Eq. 2.74 and $T_i[\mathbf{Q}(k)]$ is the Taylor expansion value in Eq. 2.73. If a number of data points that have significant weight $w_i[\mathbf{Q}(k)]$ lead to widely differing values of $T_i[\mathbf{Q}(k)]$ and $V[\mathbf{Q}(k)]$, the $\sigma^2(k)$ will be large and the PES

may be inaccurate in the neighborhood of $Q(k)$. Hence, $Q(k)$ is chosen as a new data point under this criterion.

In our applications of the Grow method, an initial PES can be generated from the data points along a reaction path, in which the single point potential energies and gradients are calculated by the DFT code and the second order derivatives are calculated with forward differences. Then, run 20 QCTs on this initial PES. New data points are selected from these recorded trajectory configurations according to the h-weight criterium and variance criterium alternately. Further details can be found in Chapter. 4.

2.5.2 Corrugation reducing procedure

The corrugation reducing procedure (CRP) developed by Busnengo and coworkers [34, 35], is implemented for the 1/2 ML Ti covered $H_2 + Ti/Al(100)$ system to obtain the PES. The CRP has been successfully employed for $H_2 +$ surface systems, *i.e.*, in H_2 dissociation on Pd(111) [34, 39, 40], Pt(111) [35, 41], Pt(211) [42, 43], Cu(111) [3, 35], Ni(100), Ni(110), Ni(111) [44], and NiAl(110) [45] surfaces.

Within the CRP, the full 6D molecule-surface potential V_{int}^{6D} is written as the sum of two 3D hydrogen atom-surface potentials R_A^{3D} and R_B^{3D} and the 6D interpolation function I^{6D} [34],

$$V_{int}^{6D}(X, Y, Z, r, \theta, \phi) = I^{6D}(X, Y, Z, r, \theta, \phi) + R_A^{3D}(X_A, Y_A, Z_A) + R_B^{3D}(X_B, Y_B, Z_B), \quad (2.80)$$

in which the six H_2 coordinates used are the hydrogen inter-molecular distance r , its center of mass coordinates (X, Y, Z) , the polar angle of orientation θ , and the azimuthal angle ϕ . The coordinates (X_A, Y_A, Z_A) and (X_B, Y_B, Z_B) are the position of two hydrogen atoms, respectively. In the CRP method, to avoid the corrugation of the PES due to the strong repulsion when the H_2 molecule is close to the metal surface, by subtracting the atomic contribution of the atom-surface potentials from V_{int}^{6D} a smooth 6D interpolation function I^{6D} can be obtained, which can be more easily interpolated.

The 3D atomic H-surface potential R_B^{3D} is given by [34],

$$R_A^{3D}(X_A, Y_A, Z_A) = I^{3D}(X_A, Y_A, Z_A) + \sum_{i=0}^n Q^{1D}(Z_i), \quad (2.81)$$

where Z_i is the distance from the H-atom to a surface site atom labeled by i , and the sum is over the n nearest neighbors. I^{3D} is the 3D interpolation function and Q^{1D} is a 1D potential.

To construct the PES, we have computed DFT data points which have been used either as input for the interpolation or for test purposes, following the same procedure as

that in the $\text{H}_2 + \text{NiAl}(110)$ [45] and $\text{H}_2 + \text{Pd}(111)$ [40] systems. The 3D interpolation function I^{3D} is obtained by a spline interpolation over Z at first and then a 2D spline interpolation over X and Y coordinates [34]. To construct the 6D interpolation function I^{6D} , the 2D cuts over (Z, r) are firstly interpolated by 2D cubic splines, and next over (θ, ϕ) by Fourier expansions, and finally over the center of mass (COM) coordinates (X, Y) by 2D cubic splines. Further details can be found in Chapter. 5.

2.6 Quasi-classical trajectory method

As already mentioned, quasi-classical trajectories are run to find and sample the dynamically relevant regions of the PES during the Grow process. When using the QCT method for reaction probability calculations, the initial rovibrational energy of the $\text{H}_2(v, j, m_j)$ molecule is taken into account by sampling the initial condition of the trajectories from a micro-canonical ensemble (conservation of the particle number and the trajectory energy). In the 6D QCT method describing H_2 dissociation on a surface, the X and Y coordinates are sampled in the unit cell (including the boundaries of the unit cell) by the Monte Carlo method,

$$\begin{aligned} X &= \xi_1 \cdot a \\ Y &= \xi_2 \cdot a \end{aligned} \quad (2.82)$$

where a is the lattice constant of the square unit cell [see Fig. 1.2 (a)], and ξ_1 and ξ_2 are two random numbers in the range of $[0, 1]$. The Z coordinate is fixed at $6.50 \text{ \AA}$ above the surface. The initial vibrational motion of the two H atoms (r coordinate) is taken into account according to a Morse potential [46]. Calculations are carried out for several different initial quantum rovibrational states (v, j, m_j) . The initial angular momentum is fixed according to $|\mathbf{L}| = \sqrt{j(j+1)}$, and the orientation of the $\mathbf{L}$ vector is selected randomly with the constraint of

$$\cos(\theta_L) = \frac{m_j}{\sqrt{j(j+1)}}, \quad (2.83)$$

where θ_L is the angle between $\mathbf{L}$ and the Z axis (which is perpendicular to the surface). The initial values of spherical polar orientation angles, θ_L and ϕ , have the form [47],

$$\begin{aligned} \xi_3 &= \frac{1}{2}(1 + \cos\theta_L) \\ \phi &= 2\pi \cdot \xi_4 \end{aligned} \quad (2.84)$$

where ξ_3 and ξ_4 are also two random numbers in the range of $[0, 1]$.

The velocities of H-atom A and B are calculated using the vector sums $\mathcal{V}_A = \mathcal{V}_z + \mathcal{V}_{vib} + \mathcal{V}_{rot}$ and $\mathcal{V}_B = \mathcal{V}_z - \mathcal{V}_{vib} - \mathcal{V}_{rot}$ respectively, in which $\mathcal{V}_z$ is the velocity in

the Z direction calculated as $\sqrt{2E_{kin}/M}$, where E_{kin} is the incidence energy and M is the mass of H_2 , and $\mathcal{V}_{vib}$ ($\mathcal{V}_{rot}$) is the contribution to the atomic velocity due to vibration (rotation). In the QCT calculations, the vibrational zero-point energy (ZPE) with a value of 0.27 eV is modelled in the trajectories. For the cartwheel rotationally excited state ($v = 0, j = 4, m_j = 0$) and helicopter rotationally excited state ($v = 0, j = 4, m_j = 4$), the initial energy of the trajectories also includes the rotational energy $E_{rot} = 0.14$ eV. For the first vibrationally excited state ($v = 1, j = 0$) the vibrational energy is set to $E_{vib} = 0.78$ eV. Normal incidence is modelled in all cases. In the CT calculations, the zero-point vibrational energy is not taken into account. Inclusion of the ZPE in the dynamics makes an adiabatic transfer of the energy from internal vibration to translation possible, a phenomenon which is called *vibrational softening*. Although this may lead to ZPE violation, the QCT method usually gives more accurate results for H_2 -surface reactions than the purely classical method [48, 49].

The quasi-classical trajectories are propagated by the velocity Verlet scheme [50, 51]. The positions and velocities from t to $t + \Delta t$ can be given by,

$$X_i(t + \Delta t) = X_i(t) + \mathcal{V}_i(t)\Delta t + \frac{\Delta t^2}{2m_H}F_i(t) \quad (2.85)$$

$$\mathcal{V}_i(t + \Delta t) = \mathcal{V}_i(t) + \frac{\Delta t}{2m_H}F_i(t) + \frac{\Delta t}{2m_H}F_i(t + \Delta t), \quad (2.86)$$

where m_H is the atomic H mass, and F_i is the force component calculated from the PESs mentioned above in Chapter 2.5.

The strict localization of the system makes the CT and QCT methods easy to implement. However, quantum effects [52] which should be important for H_2 , are not considered yet, which is the reason that we also need to calculate the H_2 dissociation probabilities by the quantum wave packet method in the next subsection to test the accuracy of the QCT and CT methods. Because of the deep molecular adsorption well in the PES, quantum effects, such as resonances or tunneling, can be especially important for the reaction dynamics.

2.7 Time-dependent wave packet method

2.7.1 Hamiltonian and the time-dependent wave packet

In the quantum dynamics treatment of H_2 -surface reactions, the six degrees of freedom (DOFs) are taken as the hydrogen intra-molecular distance r , the position of the center of mass over the unit cell (X, Y, Z), the polar angle θ and the azimuthal angle ϕ . We try to arrive at a quantum mechanical solution by solving the time-dependent Schrödinger

equation ($\hbar = 1$ in atomic units),

$$i\frac{\partial\Psi}{\partial t} = \hat{H}\Psi. \quad (2.87)$$

The 6D Hamiltonian operator $\hat{H}$ includes the kinetic energy in translation, vibration, and rotation, and the potential energy, and is given by [48]

$$\hat{H}_{6D} = -\frac{1}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{1}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu r^2} + V_{6D}(X, Y, Z, r, \theta, \phi), \quad (2.88)$$

in which M is the mass of H_2 molecule, μ is the corresponding reduced mass. V_{6D} is the 6D potential in the previous Subsection 2.5.1 and Subsection 2.5.2. Integrating over a time-step Δt , the new wave function at $(t + \Delta t)$ can be obtained,

$$\Psi(t + \Delta t) = e^{-i\hat{H}\Delta t} \cdot \Psi(t) = \hat{U}(\Delta t)\Psi(t), \quad (2.89)$$

where the unitary $\hat{U}(\Delta t) = \exp(-i\hat{H}\Delta t)$ is called the *evolution operator*. One of the strategies to propagate the wave packet is to split the time t into N small steps, $\Delta t = t/N$. Thus the whole propagation process can be written as a product of short time evolution operators,

$$\hat{U}(t) = \prod_{n=0}^{N-1} \hat{U}[(n+1)\Delta t, n\Delta t]. \quad (2.90)$$

The time-energy uncertainty principle can be considered as a limitation imposed on the propagation to determine the minimum number of points N needed in time intervals Δt with energy range ΔE [52] by,

$$\Delta t = \frac{\hbar}{2\Delta E}, \quad (2.91)$$

where $\Delta E = E_{max} - E_{min}$, the range of eigenvalues of the Hamiltonian operator, is called the *spectral range*, and $\hbar$ is the unit of the phase space. In the unconditionally stable methods, the spectral range of the initial wave packet determines the maximum size of the time step Δt .

The initial wave packet [48, 53] is given by

$$\Psi(X, Y, Z, r, \theta, \phi) = \Phi_{vj}(r)Y_{jm_j}(\theta, \phi)\frac{1}{\sqrt{A}}e^{i\vec{K}_0 \cdot \vec{R}} \int dk_z b(k_z)\frac{1}{2\pi}e^{ik_z Z}. \quad (2.92)$$

Here, $\Phi_{vj}(r)$ and $Y_{jm_j}(\theta, \phi)$ are the H_2 vibrational and rotational eigenfunctions, respectively, and v , j and m_j are the corresponding quantum numbers defined as in the QCT method (see Subsection 2.6). The initial parallel motion of the wave packet along X and Y is given in plane wave form $(1/\sqrt{A})e^{i\vec{K}_0 \cdot \vec{R}}$, in which A is the normalization factor

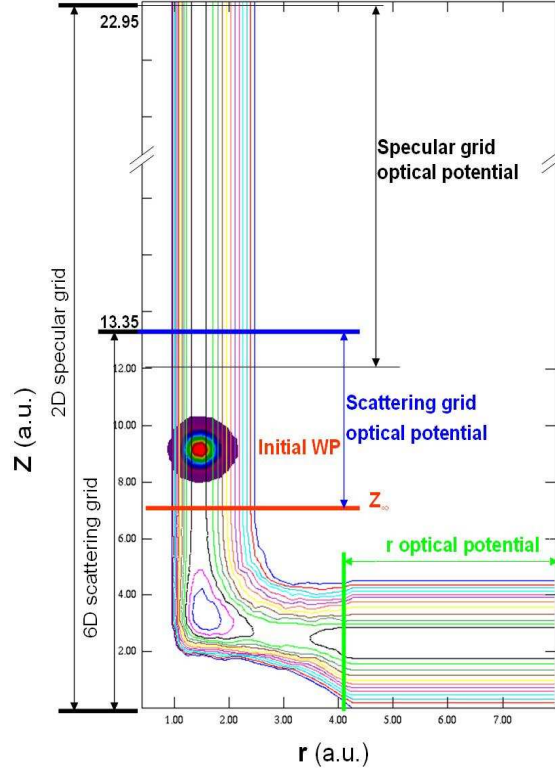


Figure 2.4: Illustration of an initial 6D wave packet projected on a two-dimensional (2D) potential energy surface. The analysis line Z_∞ , the start and end of the optical potentials are also shown.

by the surface area of the unit cell, and $\vec{K}_0$ is the initial parallel momentum at position $\vec{R}(X, Y)$. The wave packet in the Z direction has a plane wave form with initial momentum k_z , which is defined by a Gaussian distribution $b(k_z)$,

$$b(k_z) = \frac{2\zeta^2}{\pi} e^{-(k_{av}-k_z)^2\zeta^2 + i(k_{av}-k_z)Z_0}, \quad (2.93)$$

in which ζ is the width of the wave packet in momentum space, k_{av} is the average momentum and Z_0 is the center of the wave packet in Z , see Fig. 2.4.

In this thesis, the H_2 molecule with normal incidence is considered only and thus $\vec{K}_0 = 0$ and the initial distribution of the wave packet in X and Y DOFs is a flat function in Eq. 2.92.

2.7.2 Methods to propagate the time-dependent wave packet

A. The split-operator method

The pseudo-spectral method can be used to propagate the wave packet, in which the Hamiltonian is symmetrically decomposed as a non-commutative form by using the split-operator (SPO) method [53],

$$\begin{aligned} \Psi(\mathbf{x}, t + \Delta t) = & e^{-i\frac{\hat{K}_{XYZr}}{2}\Delta t} \cdot e^{-i\frac{\hat{H}_{rot}}{2}\Delta t} \\ & \cdot e^{-iV_{6D}\Delta t} \cdot e^{-i\frac{\hat{H}_{rot}}{2}\Delta t} \cdot e^{-i\frac{\hat{K}_{XYZr}}{2}\Delta t} \cdot \Psi(\mathbf{x}, t) + O(\Delta t^3), \end{aligned} \quad (2.94)$$

in which V_{6D} is the 6D PES discussed above. The 4D kinetic operator $\hat{K}_{XYZr}$ and 3D rotational operator $\hat{H}_{rot}$ are given by

$$\hat{K}_{XYZr} = -\frac{1}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{1}{2\mu} \frac{\partial^2}{\partial r^2}, \quad (2.95)$$

$$\hat{H}_{rot} = \frac{\hat{j}^2}{2\mu r^2}, \quad (2.96)$$

where $\hat{j}$ is the angular momentum operator.

Usually the algorithm is as follows: begin with a wave function in the momentum representation. Multiply point by point with $\exp(-i\frac{\hat{K}}{2}\Delta t)$ (a local operator in momentum space). Transform the result $\Phi = \exp(-i\frac{\hat{K}}{2}\Delta t)\Psi(t=0)$ to coordinate space. Now multiply point by point with $\exp(-i\hat{V}\Delta t)$. Transform the result $\Phi = \exp(-i\hat{V}\Delta t)\exp(-i\frac{\hat{K}}{2}\Delta t)\Psi(t=0)$ back to momentum space, and repeat the first step, *i.e.*, perform the pointwise multiplication $\Psi(\Delta t) = \exp(-i\frac{\hat{K}}{2}\Delta t)\Phi$.

The error per time step is proportional to Δt^3 in the SPO method and the method is unconditionally stable, *i.e.*, the maximum time step Δt is not determined by the range of eigenvalues of the Hamiltonian, but by the bandwidth of the initial wave packet. The SPO method is more efficient (requires less Hamiltonian operations per unit propagation time) than other methods. The conservation of the norm is guaranteed but the conservation of energy is not guaranteed in the SPO method.

In the application of the SPO method in this thesis, two wave packets are propagated, for the low energy range (50 – 350 meV) and the high energy range (300 – 850 meV), respectively. Superior accuracy can be obtained by using different optimized parameters for each wave packet.

2.7.3 Representation of the wave packet

The cost of propagating the wave packet depends on the cost of evaluating the action of the kinetic and potential energy operators on the wave function, which in turn depends on its representation. According to the uncertainty principle of the momentum-coordinate phase space, the volume of this phase space in units of $\hbar$ is determined by $\Delta x \Delta k \geq \hbar/2$. The lower boundary of the grid space Δx can be estimated by $\Delta x = \hbar/(2\Delta k_{max})$ [52]. Here, k_{max} is the maximum momentum, and x is a DOF represented by the Fourier method.

The discrete potential energy values and the wave packet are defined on the same grid using DVR-FBR representations. The wave function on X , Y , Z and r is represented by the Fourier representation (DVR), effectively using a plane-wave basis-set [54, 55]. The angular momentum part of the wave function is represented by a finite basis representation (FBR), using orthogonal normalized associated Legendre polynomials as basis functions. Gauss-Legendre and Fourier transformations are used to transform the wave function from the FBR to the DVR [56, 57].

An analysis line $Z = Z_\infty$ (*i.e.*, when $Z_\infty = 7.0$ a.u.) is set in gas phase above the surface where there is no molecule-surface interaction (see Eq. 2.92). Above the analysis line, a complex absorbing optical potential $e^{iV_{opt}\Delta t}$ is added in the DOF Z direction on the scattering grid to gradually damp the wave packet once it is scattered to the gas phase $Z > Z_\infty$. Another optical potential is added in the DOF r direction (*i.e.* r in the range of 4.15 – 7.975 a.u.) to damp the wave packet once H_2 is dissociated. A quadratic form optical potential [58] is employed,

$$V_{opt} = \begin{cases} A\left(\frac{Z-Z_{min}}{Z_{max}-Z_{min}}\right)^2 & \text{if } Z_{min} \leq Z \leq Z_{max} \\ 0 & \text{if } Z \leq Z_{min}, \end{cases} \quad (2.97)$$

where Z_{min} is chosen as Z_∞ and Z_{max} is chosen as the last grid point in Z (see the demonstration in Fig. 2.4), and analogously for r . The strength parameter A is chosen with respect to the incident energy E_{kin} of the initial wave packet and the length of the optical potential, such that the reflection from and transmission through the optical potential is minimal. More details can be found in Ref. [48].

Finally, the wave packet is asymptotically analyzed by the Balint-Kurti formalism [59–62]. The scattered wave packet is projected at $Z = Z_\infty$ onto the free molecular states.

A. The collocation method.

The collocation method was described by Kosloff [52]. This method considers an approximation to an arbitrary function $\Psi(x)$ using a set of functions $g_n(x)$,

$$\Psi(x) = \sum_{n=0}^{N-1} c_n g_n(x) \quad (2.98)$$

In the collocation method of Gauss the expansion coefficients c_n are found by matching the solution at N grid points using

$$\Psi(x_j) = \sum_{n=0}^{N-1} c_n g_n(x_j) \quad (2.99)$$

in which the x_j are the grid points or collocation points. A large advantage of the collocation method is that the action of the potential on the wave function is a local operation, i.e., $\hat{V}\Psi(x_j) = V(x_j)\Psi(x_j)$.

Eq. 2.99 can be written as a set of linear equations

$$\Psi_j = \sum_n G_{jn} c_n, \quad (2.100)$$

in which $\Psi_j = \Psi(x_j)$, and $G_{jn} = g_n(x_j)$. If the $g_n(x_j)$ are linearly independent the solution of Eq.2.100 is given by

$$\mathbf{c} = G^{-1}\Psi \quad (2.101)$$

The choice of the functions $g_n(x_j)$ makes the evaluation of “non-local” operations possible. For instance, the kinetic energy operator $-\frac{1}{2m}\frac{\partial^2}{\partial x^2}$ operating on grid point j becomes

$$-\frac{1}{2m}\frac{\partial^2}{\partial x^2}\Psi(x_j) = -\frac{1}{2m}\sum_{n=0}^{N-1} c_n \frac{\partial^2}{\partial x^2}g_n(x_j) \quad (2.102)$$

Of course, the choice of the grid points and of the expansion functions has a large influence on the quality of the approximation. Choosing expansion functions that obey specific boundary conditions will often help with solving the problem under consideration more efficiently.

A simplification occurs if the g_n are chosen as functions of an orthogonal basis. Using N grid points one selects as points the zeroes of $g_N(x)$. As basis functions the orthonormal functions $p_n(x)$ are taken, pre-multiplying with the weights corresponding with N -point quadrature:

$$g_n(x_j) = \sqrt{w(x)}p_n(x_j) \quad (2.103)$$

The orthogonality can then be used to find the expansion coefficients:

$$c_n = \sum_{j=1}^N \Psi(x_j) g_n(x_j) \quad (2.104)$$

The coordinate representation of the wave function on a grid of points is also called the *discrete variable representation*. The basis representation of the wave function is called the *finite basis representation* [54, 55]. Next, two collocation methods, the Fourier method and the Gaussian quadrature method, are discussed.

B. The Fourier representation

Plane-wave basis sets $e^{ik \cdot x}$ can be chosen for the $g_n(x)$ functions in Eq. 2.98 of the collocation method, using what is called a *Fourier representation*. For N equally spaced discrete points over an interval $x = [0, L]$, we have $g_n(x)$ functions

$$g_n(x) = \frac{1}{\sqrt{N}} e^{i2\pi n x/L}, \quad (2.105)$$

where $n = -(L/2 - 1), \dots, 0, \dots, L/2$, and N is the normalization factor. The plane wave basis sets are mutually orthogonal,

$$\sum_{n=0}^{N-1} e^{-\frac{i2\pi p x}{L}} e^{\frac{i2\pi q x}{L}} = N \delta_{p,q} \quad (2.106)$$

where p and q are integers. They are also the eigenfunctions of the kinetic operator *i.e.*,

$$\nabla_x^2 e^{ik \cdot x} = -k^2 e^{ik \cdot x}. \quad (2.107)$$

Using the plane wave basis sets, the wave function in Eq. 2.98 along x can be given by,

$$\psi(x_j) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} c_n e^{i2\pi n x/L}, \quad (2.108)$$

where c_n is the weight coefficient of the plane wave with momentum $2\pi n/L$ and it can be obtained by inverting of Eq. 2.108 as

$$c_n = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \psi(x_j) e^{-i2\pi n x/L}. \quad (2.109)$$

Eq. 2.108 and Eq. 2.109 are known as *Fourier transformations* (FTs), the effort of which scales as N^2 . In applications, the *Fast Fourier transformation* (FFT) method is employed which has a computational scaling of $N \log_2 N$ for suitable values of N [22, 63]. The kinetic energy operator in X , Y , Z and r (see the Hamiltonian in Eq. 2.95) involves calculating the second order derivatives of the wave function. Thus the wave function in these degrees of freedom can be represented by the Fourier representation.

C. Gauss-Legendre discrete variable representations

The angular momentum part of the wave function can be represented by the discrete variable representations (DVR) [54, 55], in which the spherical harmonics $Y_{jm_j}(\theta, \phi)$ are used as basis functions,

$$Y_{jm_j}(\theta, \phi) = N(j, m_j) P_j^{m_j}(\cos\theta) e^{im_j\phi} \quad (2.110)$$

where $P_j^{m_j}(\cos\theta)$ is an associated Legendre polynomial, and $N(j, m_j)$ is a normalization factor, such that

$$\int_0^{2\pi} \int_0^\pi Y_{jm_j} Y_{j'm'_j}^* \sin\theta d\theta d\phi = \delta_{jj'} \delta_{m_j m'_j}. \quad (2.111)$$

The spherical harmonics $Y_{jm_j}(\theta, \phi)$ are the eigenfunctions of the rotational kinetic energy operator in Eq. 2.95

$$\frac{\hat{j}^2}{2\mu r^2} Y_{jm_j}(\theta, \phi) = \frac{j(j+1)}{2\mu r^2} Y_{jm_j}(\theta, \phi). \quad (2.112)$$

Accuracy in this representation can be achieved by taking the grid points in θ as roots of the Legendre polynomial $P_{j_{max}+1}(\cos\theta)$ as in Eq. 2.103, where j_{max} is the highest j quantum number of the spherical harmonic basis sets. The transformation from the DVR to the FBR is accomplished by means of an unitary transformation matrix,

$$\psi(\theta_i) = \sum_j c_n T_{in}, \quad (2.113)$$

where c_n is given by

$$c_n = \sum_j T_{in} \psi(\theta_i), \quad (2.114)$$

and the elements of the transformation matrix T_{in} are given by

$$T_{in} = \sqrt{w(x_j)} L_i(x_j). \quad (2.115)$$

The ϕ -dependence of the spherical harmonics involves the terms of $e^{im_j\phi}$. There a Fourier representation can be used for the grid of ϕ . The basis representation of the wave function in θ and ϕ using spherical harmonics is a non-direct product representation. Gauss-Legendre and Fourier transformations are used to transform the wave function from the non-direct FBR representation to the direct product DVR representation in the degrees of freedom θ and ϕ .

2.7.4 Asymptotic analysis

The wave function should describe the physical situation in which a bundle of molecules in one specific initial vibration-rotation state (v, j, m_j) and with a narrowly defined initial kinetic energy [64–66]

$$E_{kin} = \frac{1}{2M}k^2 \quad (2.116)$$

scatters from a surface, under normal incidence (the incidence angle with the surface is 90 degrees, the theory is easily extended to the case of non-normal incidence). In Eq.2.116, M is the mass of the molecule, and k the value of the momentum of the molecule in the direction perpendicular to the surface. The molecules are scattered with conservation of the energy from (v, j, m_j) to (v', j', m'_j, n, m) state (normal incidence):

$$\begin{aligned} E &= E_{kin}(v) + E_{vib}(v) + E_{rot}(j, m_j) \\ &= E'_{kin}(v') + E'_{vib}(v') + E'_{rot}(v', j') + E_{dif}(n, m) \end{aligned} \quad (2.117)$$

$$E'_{kin} = \frac{1}{2M}k_{v'j'm'_jnm}^2 \quad (2.118)$$

$$E_{dif}(n, m) = \frac{1}{2M}(n^2G_X^2 + mG_Y^2) \quad (2.119)$$

In Eq.2.118 $k_{v'j'm'_jnm}$ is the momentum along Z of the molecule that is scattered to the state described by $(v'j'm'_jnm)$. Note that the initial (final) values of the vibrational and rotational energy depend on v and j (v' and j'). In addition, we will impose conservation of flux: at an arbitrary distance to the surface the flux of the ingoing molecules is equal to the flux of the scattered molecules, for the case that only inelastic scattering occurs. Under these conditions we can write the following expression for the *stationary wave function*, for a distance to the surface $Z = Z_\infty$ so that molecule and surface no longer interact with each other:

$$\begin{aligned} &\Psi^+(E|Z_\infty, X, Y, r, \theta, \phi) \\ &= \frac{e^{-ikZ_\infty}}{\sqrt{2\pi}}\phi_{vj}(r)\sqrt{\frac{1}{L_X L_Y}}Y_{jm_j}(\theta, \phi) \\ &\quad - \sum_{v'j'm'_jnm} \sqrt{\left|\frac{k_{vjm_j}}{k_{v'j'm'_jnm}}\right|} S_{vjm_jnm \rightarrow v'j'm'_jnm}(E) \cdot \frac{e^{-ik_{v'j'm'_jnm}Z_\infty}}{\sqrt{2\pi}}\phi_{vj}(r) \cdot \\ &\quad Y_{j'm'_j}(\theta, \phi)\sqrt{\frac{1}{L_X L_Y}}e^{i(nG_X X + mG_Y Y)}. \end{aligned} \quad (2.120)$$

In Eq.2.120, $\phi_{vj}(r)$ is a vibration wave function normalized on r , and $Y_{j'm'_j}(\theta, \phi)$ is the normalized spherical harmonic describing the rotation of a molecule. By pre-multiplying

the plane wave function $e^{i(nG_X X + mG_Y Y)}$ with $\sqrt{\frac{1}{L_X L_Y}}$, the stationary wave function is normalized on the surface unit cell. The S-matrix is a symmetric, unitary matrix, from which scattering probabilities can be obtained.

The asymptotic value of Z_∞ is larger than 7.0 bohr, where the interaction between the molecule and the surface is negligible. The wave packet is analyzed by the Balint-Kurti method [59–62], in which the wave packet is projected at $Z = Z_\infty$ onto the free particle states:

$$C_{nm\nu jm_j}(Z_\infty, t) = \int \Psi(Z_\infty, r, x, y, \theta, \phi; t) \Phi_{nm\nu jm_j}^*(r, x, y, \theta, \phi) d\tau, \quad (2.121)$$

where $d\tau$ is an integration element and

$$\Phi_{nm\nu jm_j}^*(r, x, y, \theta, \phi) = \phi_{\nu j}(r) \frac{e^{i(\mathbf{K}^0 + \mathbf{G}_{nm}) \cdot \mathbf{R}}}{\sqrt{A}} Y_{jm_j}(\theta, \phi). \quad (2.122)$$

In this equation $e^{i(\mathbf{K}^0 + \mathbf{G}_{nm}) \cdot \mathbf{R}} / \sqrt{A}$ is a plane wave translational wave function in x and y with diffraction quantum numbers n and m , which is normalized on the surface unit cell with area A .

After the propagation is completed, the time-dependent coefficients $C_{nm\nu jm_j}(Z_\infty, t)$ are Fourier transformed from the time to the energy domain

$$A_{nm\nu jm_j}(E) = \int_0^T e^{iEt/\hbar} C_{nm\nu jm_j}(Z_\infty, t) dt. \quad (2.123)$$

The probability for a transition from the initial state with rotational quantum numbers (j_0, m_{j0}) , vibrational quantum number ν_0 , and initial translational momenta k_Z, k_x and k_y to the final state $(nm\nu jm_j)$, is then given by

$$P = |S(nm, \nu, j, m_j | \nu_0 j_0 m_{j0} | k_x, k_y, -k_Z)|^2. \quad (2.124)$$

The S -matrix elements $S(nm, \nu, j, m_j | \nu_0 j_0 m_{j0} | k_x, k_y, -k_Z)$ are given by

$$S(nm, \nu, j, m_j | \nu_0 j_0 m_{j0} | k_x, k_y, -k_Z) = \delta_{0n} \delta_{0m} \delta_{\nu_0 \nu} \delta_{j_0 j} \delta_{m_{j0} m_j} e^{-i2k_Z Z_\infty} - \left(\frac{k_Z k_{nm\nu j}}{2\pi} \right)^{1/2} \frac{\hbar e^{-ik_{nm\nu j} Z_\infty}}{Mb(-k_z)} A_{nm\nu jm_j}(E), \quad (2.125)$$

where $k_{nm\nu j}$ is the final momentum in the Z -direction of the molecule with final quantum numbers n, m, ν and j . The first term on the right-hand side of Eq.2.125 involving the Kronecker delta functions cancels the contribution from the incident wave function to the time-integral in Eq.2.123.

The scattering probability at an incident energy E_{kin} for a transition from the initial state to the final state can be obtained from the S-matrix by [48],

$$P_{vj m_j \rightarrow v' j' m'_j nm}(E_{kin}) = |S_{vj m_j \rightarrow v' j' m'_j nm}(E_{kin})|^2. \quad (2.126)$$

Thus the reaction probability at an incident energy E_{kin} is given by summing up all the scattering probabilities and then subtracting from 1,

$$P_r(E_{kin}) = 1 - \sum_{v' j' m'_j nm} P_{vj m_j \rightarrow v' j' m'_j nm}(E_{kin}). \quad (2.127)$$

2.8 Transition state theory

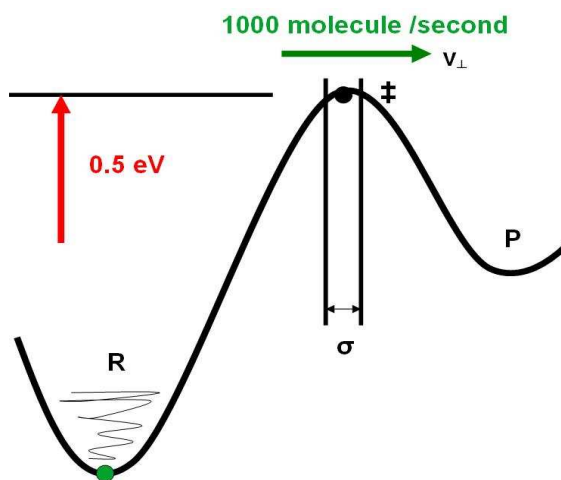


Figure 2.5: A reaction with a barrier height of 0.50 eV. “R”, “‡” and “P” indicate the reactant, saddle point and the product, respectively. The two vertical lines indicate the dividing surface between R and P with a thickness of σ , and $v_{\perp}$ is the flux out of the transition state.

After the reaction path, the saddle point and the PES of a reaction along the reaction path are obtained, we can calculate the reaction rate constant (or coefficient) at a given temperature (T). In applying transition state theory (TST) to $H_2 + \text{Ti}/\text{Al}(100)$ systems, we assume that the nuclear dynamics takes place on the ground state PES and the BO approximation holds (see also Section 2.1). A typical reaction with a barrier of 0.50 eV occurs 1000 times per second at room temperature, see Fig. 2.5. The transition over the barrier is much slower than the vibrations and can be regarded as a rare event. We assume that the nuclear dynamics can be treated by classical mechanics [67–71]. Rather than the

microcanonical ensemble $\Omega(N, V, E)$, the canonical ensemble $Q(N, V, T)$ is used in TST, in order to calculate the partition function through $e^{-E/k_B T}$, where N is the number of particles, V is the volume, E is the energy of the state and k_B is the Boltzmann constant. Thus, the system under investigation must be at thermal equilibrium in the reactant valley.

According to the Boltzmann distribution, the probability of being in the transition state can be given through the configuration integrals (or partition functions),

$$P_{\ddagger} = \frac{\int_{\ddagger} e^{-V(\mathbf{x})/(k_B T)} d\mathbf{x}}{\int_R e^{-V(\mathbf{x})/(k_B T)} d\mathbf{x}} \equiv \frac{Z_{\ddagger}}{Z_R}. \quad (2.128)$$

where $V(\mathbf{x})$ is the potential function and $\mathbf{x}$ is the coordinate. In kinetic theory [72], the average speed of particles moving from left to right is

$$\begin{aligned} \langle \mathcal{V}_{\perp} \rangle &= \frac{\int_0^{\infty} \mathcal{V} e^{-\mu_{\perp} \mathcal{V}^2 / (2k_B T)} d\mathcal{V}}{\int_{-\infty}^{\infty} e^{-\mu_{\perp} \mathcal{V}^2 / (2k_B T)} d\mathcal{V}} \\ &= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}}, \end{aligned} \quad (2.129)$$

where $\mu_{\perp}$ is the mass of the particle. If the dividing surface can be regarded as an one-dimensional box with thickness σ , the frequency of a complex at $\ddagger$ passing over the barrier is this averaged speed divided by σ :

$$\nu = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{1}{\sigma}. \quad (2.130)$$

The way of calculating ν indicates that recrossings of the transition state are neglected, which is a severe assumption in TST. The TST reaction rate constant can be calculated from the probability $P_{\ddagger}$ and the frequency ν ,

$$\begin{aligned} k^{TST}(T) &= \frac{\sigma \int_{\ddagger} e^{-V_{SP}(\mathbf{x})/(k_B T)} d\mathbf{x}}{\int_R e^{-V_R(\mathbf{x})/(k_B T)} d\mathbf{x}} \nu \\ &= \frac{\sigma \int_{\ddagger} e^{-V_{SP}(\mathbf{x})/(k_B T)} d\mathbf{x}}{\int_R e^{-V_R(\mathbf{x})/(k_B T)} d\mathbf{x}} \frac{\langle \mathcal{V}_{\perp} \rangle}{\sigma} \end{aligned} \quad (2.131)$$

$$= \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R}, \quad (2.132)$$

where V_R and V_{SP} are the potential energy at R and the saddle point, respectively. Using the harmonic approximation, the PES can be Taylor expanded to find the normal modes

at R and $\ddagger$ (the first order derivatives are zeros):

$$V_R(\mathbf{x}) = V_R + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i} \mathbf{x}_{R,i}^2 \quad (2.133)$$

$$V_{SP}(\mathbf{x}) = V_{SP} + \sum_{i=1}^{3N} \frac{1}{2} k_{SP,i} \mathbf{x}_{SP,i}^2, \quad (2.134)$$

where the $k_{R,i}$ and $k_{SP,i}$ are the second derivative of the modes respectively at R and at the saddle point $\ddagger$. Thus, the vibrational frequency of a mode can be give by

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}. \quad (2.135)$$

Substituting V_R and V_{SP} in Eq. 2.131 by the above Taylor expansion and $\sqrt{k/\mu}$ by frequency in Eq. 2.135, the rate constant from harmonic transition state theory (hTST) is give by

$$k^{hTST}(T) = \frac{\prod_{i=1}^{3N} \nu_{R,i}}{\prod_{i=1}^{3N-1} \nu_{SP,i}} e^{-\frac{V_{SP}-V_R}{k_B T}}. \quad (2.136)$$

Because recrossings are not considered in TST, the rate constant k^{TST} overestimates the exact reaction rate. The event of once crossing and recrossing should not contribute, but is counted as a reaction event in TST. The variational principle can be used to optimize the location and shape of the dividing surface that provides the smallest value of the rate constants [73]. The variational transition state theory (VTST) rate coefficient k^{VTST} is the one that minimizes the TST rate constant k^{TST} in Eq. 2.136,

$$k^{VTST}(T) = \kappa k^{TST}(T), \quad (2.137)$$

where κ can be determined by the Wigner-Keck-Eyring (WKE) procedure, by running trajectories from the transition state [73–75]. In the H_2 –surface systems, κ is close to 0.5 [71].

2.9 Molecular beam simulations

In experimental studies of H_2 dissociation on surfaces, supersonic molecular beams are often employed [37, 76, 77], in which H_2 molecules are in a non-Boltzmann rovibrational state population with a distribution of incidence energies. Thus different rovibrational states and a distribution of the collision energies should be considered.

2.10 References

In H₂ molecular beam (MB) experiments [37, 76, 77], the averaged collision energy $\langle E_{kin} \rangle$ depends on the nozzle temperature (T_n) with $E_{kin} \approx 2.5 k_B T_n - 2.7 k_B T_n$, vibrational energy $E_{vib} = k_B T_n$, and a rotational energy $E_{rot} \approx 0.8 k_B T_n$ [77, 78], (k_B is the Boltzmann constant). Note that the gas phase rotational energy E_{rot} dependence on the temperature is $k_B T$. The distribution of velocity $\mathcal{V}_z$ in the MB for various nozzle temperatures can be obtained from time-of-flight mass spectrometry, and obeys a distribution [37, 77, 79, 80],

$$f(\mathcal{V}_z; T_n) = C \mathcal{V}_z^3 e^{-\frac{(\mathcal{V}_z - \mathcal{V}_0)^2}{\alpha^2}}, \quad (2.138)$$

where C is a constant, $\mathcal{V}_0$ is the nozzle temperature dependent stream velocity, and α is the width of the velocity distribution. The population of a rovibrational state (v, j) in the MB can be given approximately by,

$$F_B(v, j, T_n) = e^{-E_{vib}(v)/kT_n} w(j) (2j + 1) e^{-E_{rot}^v(j)/0.8kT_n} / N, \quad (2.139)$$

where $w(j)$ is a weight function for H₂ nuclear spin statistics [$w(j) = 1$ for even j values and $w(j) = 3$ for odd j]. N is the normalization factor,

$$N = \sum_{v,j} e^{-E_{vib}(v)/kT_n} w(j) (2j + 1) e^{-E_{rot}^v(j)/0.8kT_n}. \quad (2.140)$$

Thus the energy resolved reaction probability is calculated from,

$$R(E_{kin}; T_n) = \sum_{v,j} F_B(v, j, T_n) R(E_{kin}; v, j), \quad (2.141)$$

where $R(E_{kin}; v, j)$ is the reaction probability from QCT results. The simulated MB reaction probability $R(T_n)$ is equal to the energy-resolved reaction probability $R(E_{kin}; T_n)$ convoluted with the velocity distribution in Eq. 2.138:

$$R(T_n) = \frac{\int_0^\infty f(\mathcal{V}_z; T_n) R(E_{kin}; T_n) d\mathcal{V}_z}{\int_0^\infty f(\mathcal{V}_z; T_n) d\mathcal{V}_z}. \quad (2.142)$$

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Chapter 3

A DFT study of H₂ reacting on Ti/Al(100) surfaces

This chapter is based on:

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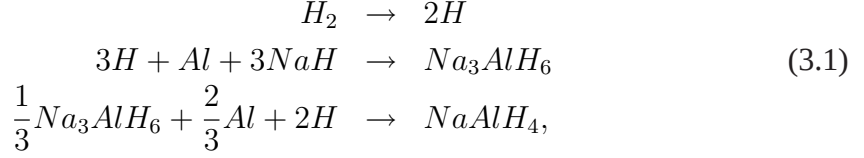
Abstract

Using density functional theory, we study H₂ dissociation on Ti/Al(100) alloy surfaces, modelled by different Ti coverages varying from 1/4 to 1 monolayer. The minimum barrier height for H₂ dissociation depends on the specific Ti coverage on the Al surface. In view of experimental information on Ti in hydrogenated and dehydrogenated NaAlH₄, the most realistic model promoting H₂ dissociation is found to be the (100) surface of Al covered by 1 monolayer of Ti in a c(2 × 2) structure, with Ti atoms in the first and third layers. This model has a late dissociation barrier with a height of only 0.23 eV, preceded by a deep molecular chemisorption well with a well depth of 0.45 eV. The projected density of states analysis provides a molecular orbital view in which the barrier-less approach to the molecular chemisorption well is mainly explained by an occupied-virtual attraction between the H₂ σ_g and Ti $3d_{z^2}$ orbitals. The barrier separating the molecular chemisorption well and the dissociated state can be understood as resulting from a competition between increasing overlap of the H₂ σ_u and Ti $3d_{xz}$ orbitals and decreasing overlap of the H₂ σ_g and Ti $3d_{z^2}$ orbitals.

3.1 Introduction

One of the questions in hydrogen storage that remains open is how catalysts like Ti improve the kinetics and reversibility of hydrogen absorption in and release from the complex metal hydride sodium alanate (NaAlH₄), which has emerged as a model system. This

storage process can, in principle, be envisaged to take place through the following three steps [1],



which can be summarized as,



Recent isotope exchange experiments [2] on both absorption and desorption of H_2 in Ti-doped $NaAlH_4$ suggest that diffusion of heavier hydrogen-containing species, such as AlH_x or NaH , represents the rate limiting step in H_2 release and uptake. However, it seems likely that Ti should also catalyze H_2 dissociative adsorption (and the reverse process, associative desorption).

Theoretically, molecular hydrogen dissociation on pure Al surfaces is found to be kinetically unfavorable. The lowest energy barriers for H_2 dissociation on pure Al surfaces are 1.05 eV on Al(100) [3], and 0.70 eV on Al(110) [4]. As further discussed below, Ti/Al(100) surfaces represent a sensible choice for modeling H_2 dissociation on Al with Ti in it, and several Al(100) surfaces with low Ti coverages have been studied theoretically [3, 5, 6]. This chapter thus focuses on constructing a reasonable Ti/Al(100) surface model to address the catalytic role played by titanium in hydrogenation and dehydrogenation of $NaAlH_4$.

The fcc Ti lattice constant obtained from first-principles band-structure calculations [7] is found to be $a = 4.08 \text{ \AA}$, which is very close to the theoretical fcc Al lattice constant, $a = 4.04 \text{ \AA}$ [3, 8]. Although the fcc phase of Ti cannot be found at any temperature in nature, matchable lattice constants make the pseudomorphic growth of an fcc Ti phase on Al(100) favorable at low Ti coverage [9, 10]. Low-energy electron diffraction (LEED) experiments by Kim *et al.* [9] show that, at low Ti coverage, Ti atom deposition on a clean Al(100) surface exhibits a $c(2 \times 2)$ pattern, with the Ti atoms probably residing in the second layer of the substrate. Low-energy ion scattering (LEIS) measurements by Saleh *et al.* [10] confirm that the surface Al atoms do indeed float on top of the Ti film at low Ti coverage, up to 1/2 monolayer (ML), because the initial Ti deposition does not change the LEIS results. When the Ti coverage is increased further, Ti adatoms are instead incorporated also into the top layer of the Al substrate. For instance, the fact that half of the Al LEIS peak area remains after 2 ML Ti deposition [11], together with the LEED experiments [9], suggests that in this case a $c(2 \times 2)$ -Ti/Al(100) alloy surface is formed, in which half of the top layer is composed of Ti atoms. Due to the limitation that LEIS experiments can only probe the surface top layer, nothing is known experimentally about the layers underneath.

The effect of Ti alloying with the Al(100) surface on H₂ dissociation barriers has been theoretically studied by Muckerman and coworkers [5], and by Smith and coworkers [3]. Muckerman and coworkers used density functional theory (DFT) at the generalized gradient approximation (GGA) level with the RPBE functional [12] to study the effect of coverages varying from 1/8 to 1/2 ML, with Ti atoms present in the first top layer and/or the second layer of the slabs being investigated. The minimum barrier was found to be 1.62 eV for H₂ dissociating on a 1/2 ML Ti/Al(100) surface with Ti in the top layer, whereas dissociation was found to be non-activated on a 1/4 ML reconstructed Ti/Al(100) surface, with Ti also present in the first layer. A Ti/Al(100) surface of even lower coverage (1/18 ML Ti) has been studied [3] by Smith and coworkers using DFT at the GGA level with the PBE functional [13], who found that the H₂ dissociation on this surface is also non-activated.

Extended X-ray absorption fine structure (EXAFS) experiments in Ref. [5] show that in hydrogenated and dehydrogenated NaAlH₄ Ti is in an environment where nearest neighbor Ti-Ti distances are 3.80 Å. This is in agreement with our computational finding that the first and the third layer Ti-Ti distance is 3.80 Å in the 1 ML Ti coverage structure reported below. In contrast, for the 1/4 ML Ti/Al(100) surfaces modelled in Refs. [5, 6] the nearest neighbor distance between Ti atoms exceeds 5.0 Å.

Motivated by this discrepancy between the Ti-coverage promoting H₂ dissociation according to the work of Muckerman and coworkers and the Ti-coverage suggested by the EXAFS experiments, we consider mainly two questions in the present work. First, what are the best slab models for representing (100) type alloy surfaces for higher Ti coverages, ranging from 1/2 to 1 ML? Second, what are the minimum barrier heights for H₂ dissociation on the surfaces thus modelled, taking into account that transition metal doping can dramatically decrease such barriers? To answer these questions, DFT calculations are performed within the GGA, employing the PW91 functional [14].

We find that the minimum barrier height for H₂ dissociating on the pure Al(100) surface is 0.96 eV. On the 1/2 ML Ti/Al(100) surface with Ti atoms in the second layer, the minimum barrier height is 0.63 eV. The most realistic model promoting dissociation we find is a 1 ML Ti/Al(100) surface, with Ti in the first and the third layer, which has a late minimum barrier of only 0.23 eV and a deep molecular chemisorption well of -0.45 eV in front of the late barrier in the reaction path. In the 1 ML model, the first layer and the third layer Ti-Ti distance is consistent with the EXAFS results referred to above [5]. Therefore, we have been able to come up with a model in which not only Ti catalyzes H₂ dissociation, but in which the local structure around Ti is also in agreement with the existing experiments. We also report some results of calculations on H₂ dissociation on 1/4 ML Ti/Al(100) surfaces, to compare with the work of Muckerman and coworkers [5, 6].

This chapter is organized as follows. The methodology and numerical details are

presented in Section 3.2, and the stability of Ti in Al(100) for different coverages and structures is discussed in Section 3.3.1. Section 3.3.2 discusses the H_2 dissociation barriers computed for different Ti/Al(100) surfaces and Section 3.3.3 provides an analysis of the local chemical reactions during H_2 dissociation. Section 3.4 concludes the chapter.

3.2 Methodology and numerical details

The DFT code DACAPO [15] is used to study H_2 dissociation on different $c(2 \times 2)$ slab models. The PW91 functional [14], which has been shown to give good results for H_2 dissociating on the NiAl(110) alloy surface [16, 17], is employed to describe the exchange-correlation energy of the electrons. The PW91 functional should give results similar to the PBE functional [13] used in Ref. [3] to study H_2 dissociation on a $1/18$ ML Ti/Al(100) surface, because the PBE functional was designed to reproduce PW91 energies [13]. We also tested the RPBE functional [12] used in Refs. [5, 6], and found it typically gives higher barriers than the PW91 functional, by about 0.25 eV. This is in accordance with recent theoretical research on $H_2 + Ru(0001)$, where the RPBE dissociation barrier heights were likewise larger than the PW91 barrier heights [18]. Subsequent experimental research [19] showed that the real barrier heights should fall in between the PW91 and RPBE values with neither functional performing better on $H_2 + Ru(0001)$. The ion cores are described by ultrasoft pseudopotentials [20], with core cutoff radii of $r_c^H = 0.46$ Å, $r_c^{Al} = 0.84$ Å and $r_c^{Ti} = 1.16$ Å. A plane wave basis set is used for the electronic orbitals, with cutoff energy 400 eV. The Brillouin zone is sampled by the Monkhorst-Pack [21] method, using a set of $12 \times 12 \times 1$ k -points. Performing tests with both spin-polarized and spin-unpolarized calculations shows that spin-unpolarized calculations can be used to compute the potential energies reported in this chapter.

Starting from bulk Al, the fcc lattice constant we get for aluminum is $a = 4.04$ Å, which is in excellent agreement with both theoretical [3, 8] (4.04 Å) and experimental results [22] (4.05 Å).

Next, pure Al(100) slabs were built, using 4 to 8 layers with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell. The slab interlayer distances (initially $a/2$) were relaxed by applying the quasi-Newton (QN) minimization method in the slab optimization, while they were subsequently kept fixed at their relaxed values in the calculations on H_2 dissociation. The maximum force allowed in the QN optimization was set to 0.01 eV/Å. A vacuum layer of 15.0 Å was placed between the slabs in the Z direction to avoid artificial interactions caused by the periodic boundary conditions. The $c(2 \times 2)$ -Ti/Al(100) slabs are obtained by replacing half of the Al atoms by Ti atoms in a specific layer (layers) with a $c(2 \times 2)$ pattern. Using the above parameters and slabs, the energies are converged to within 0.1 eV and the slab geometries are converged to within 0.01 Å, based on tests of adding more Al layers at the bottom of the 4-layer slab, going from 4 layers to 8 layers.

The H_2 dissociation barrier heights presented below are obtained using the nudged elastic band (NEB) method [23, 24]. Both initial and final configurations have the same center of mass (COM) X and Y coordinates of the H_2 molecule. In all initial H_2 gas phase configurations, H_2 is 4.0 Å above the surface, and parallel to the surface with a bond length of 0.755 Å. Final dissociated H-H configurations describe the relaxed atomic chemisorption minima on the slab. For the pure Al(100) slab, the COM of H_2 is at the hollow site. The final geometry is two hydrogen atoms that occupy neighboring bridge sites. For the 1/2 ML Ti/Al(100) surface with Ti in the second layer, the COM of H_2 is at the bridge site. The dissociated hydrogen atoms occupy two neighboring Al top sites. For 1 ML and other 1st layer Ti coverages, the COM of H_2 is at the Ti site, with the two hydrogen atoms pointing to the Ti-Al neighboring bridge sites. To obtain reaction paths, three images are linearly interpolated and equally spaced between the initial and final configurations. Artificial spring forces are added between the adjacent images. The QN minimization is performed both on the component of the spring forces tangent to the reaction path, and on the component of the real Coulomb forces orthogonal to the reaction path, converging the forces to within 0.05 eV/Å.

To understand the mechanism of H_2 dissociation, the two-center projected density of states (PDOS) is calculated at energies ε of the localized orbital ϕ_a , as

$$n_a(\varepsilon) = \sum_i \sum_k |\langle \phi_a | \psi_{ik} \rangle|^2 \delta(\varepsilon - \varepsilon_{ik}), \quad (3.3)$$

where i runs over all electronic bands, and k labels the $\mathbf{k}$ -points used for sampling the Brillouin zone. The ψ_{ik} are the Kohn-Sham wave functions and the ε_{ik} are the corresponding eigenvalues. The Fermi level is taken as the energy zero. The δ function is Gaussian expanded with a width of 0.20 eV. The ϕ_a can be chosen as the H_2 molecular bonding (σ_g) and antibonding (σ_u) orbitals, which are constructed as the normalized linear combinations of hydrogen s orbitals, ϕ_s^H , centered at the positions of the two hydrogen atoms $\mathbf{R}_1$ and $\mathbf{R}_2$:

$$\phi_{\sigma_g}(\mathbf{r}) = c_1 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) + \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (3.4)$$

$$\phi_{\sigma_u}(\mathbf{r}) = c_2 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) - \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \quad (3.5)$$

where $c_1 = 1/\sqrt{2(1+S)}$, $c_2 = 1/\sqrt{2(1-S)}$ are the normalization coefficients, and S is the overlap term $S = \int \phi_s^{H*}(\mathbf{r} - \mathbf{R}_1) \phi_s^H(\mathbf{r} - \mathbf{R}_2) d\tau$, which is analytically calculated by [25, 26],

$$S = \left\{ 1 + \frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} + \frac{1}{3} \left(\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} \right)^2 \right\} e^{-|\mathbf{R}_1 - \mathbf{R}_2|/a_0}, \quad (3.6)$$

where a_0 is the Bohr radius.

3.3 Results and discussion

3.3.1 Slab models

In this subsection, three 4-layer slab models have been introduced to study H_2 dissociation: Model-1, the pure Al(100) surface; Model-2, the 1/2 ML $c(2 \times 2)$ -Ti/Al(100) surface with Ti present in the second layer [Fig. 3.1(a)]; and Model-3, the 1 ML $c(2 \times 2)$ -Ti/Al(100) surface with Ti present in the first and third layers [Fig. 3.1(c)].

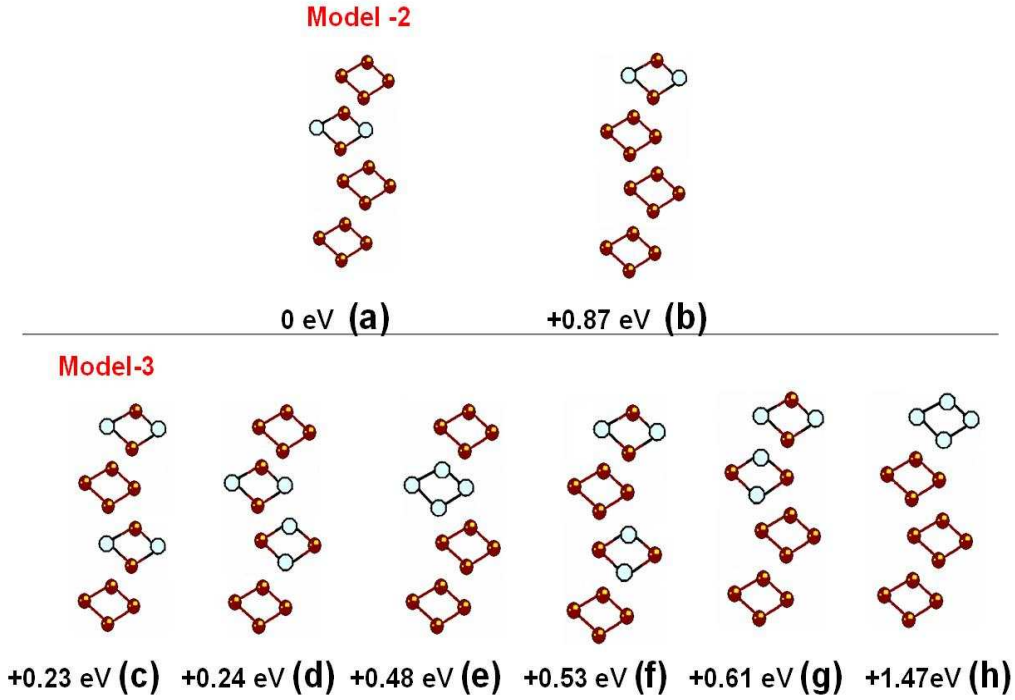


Figure 3.1: Possible structures for 1/2 ML (a - b) and 1 ML (c - h) Ti/Al(100) with $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface unit cells. Ti binding energies are listed below the structures. Structure (a) is taken as the energy zero. The brown and light blue spheres represent Al and Ti atoms, respectively.

For a Ti coverage of 1/2 ML, we computed two possible $c(2 \times 2)$ -Ti/Al(100) structures. In the first structure (Model-2), half of the Al atoms in the second layer of Al(100) are replaced by Ti atoms, Fig. 3.1(a). In the second structure, half of the Al atoms in the first layer are replaced by Ti atoms, Fig. 3.1(b). We find that the second layer surface alloy [Fig. 3.1(a)] has a much lower Ti binding energy (is more stable) by 0.87 eV/Ti atom than the first layer surface alloy [Table 3.1 and Fig. 3.1(b)]. Here, the binding energy per Ti atom is defined by

$$E_{binding}^{Ti} = (E_{slab}^{Ti_nAl} - E_{slab}^{Al})/n, \quad (3.7)$$

in which $E_{slab}^{Ti_nAl}$ and E_{slab}^{Al} are the Ti/Al(100) and pure Al(100) slab energies, respectively, and n is the number of Ti atoms in the surface unit cell. The Ti binding energy of the structure in Fig. 3.1(a) is taken as the energy zero. The lower binding energy of the 1/2 ML slab with Ti in the second layer indicates that initial Ti deposition does not change the surface Al layer. The Ti atoms deposit into the subsurface layer to form a $c(2 \times 2)$ pattern, which agrees with the experimental [9, 10] and with previous computational results [5].

For a Ti coverage of 1 ML, the configurations shown in Fig. 3.1(c - h) are considered. We find that the so-called $L1_2$ surface alloy (Model-3) is the most stable one, in which 1/2 ML Ti is in the first layer and another 1/2 ML Ti is in the third layer, [Ti binding energy 0.23 eV/Ti atom, Table 3.1 and Fig. 3.1(c)]. In this 4-layer $L1_2$ structure, the third layer Ti atoms are underneath the first layer Ti atoms, making the slab more stable (by about 0.30 eV/Ti atom) than the so-called 4-layer $D0_{22}$ structure, Fig. 3.1(f). However the $D0_{22}$ crystal is slightly more stable than the $L1_2$ crystal of bulk $TiAl_3$ [27]. The fact that, in contrast, the 4-layer $L1_2$ slab is more stable than the $D0_{22}$ 4-layer slab, has been explained from bonding interactions between the first layer Ti atoms and the third layer Ti atoms [28]. The 2, 3-layer doped slab [Fig. 3.1(d)] is almost as stable as the 1, 3-layer doped slab [Fig. 3.1(c)]. Because the 2, 3-layer doped slab would be expected to be the same as the 1/2 ML Ti/Al(100) slab of Fig. 3.1(a) from the viewpoint of an approaching H_2 molecule, we do not consider this model further.

From our DFT results, the distances of layers containing Ti to nearby Al layers in Ti/Al(100) slabs may differ considerably from the corresponding interlayer distances in a pure Al slab. In the 4-layer pure Al(100) slab (Model-1), the distances between layers 1 and 2, and layers 2 and 3 are 2.07 Å and 2.05 Å, respectively [see Table 3.2 and Fig. 3.2(a)]. As shown in Table 3.2 and Fig. 3.2(b) for the 4-layer 1/2 ML $c(2 \times 2)$ -Ti/Al(100) alloy slab (Model-2), the distances between layers 1 and 2 and layers 2 and 3 are quite close to the bulk Al layer distance of 2.02 Å, smaller than those in the 4-layer Al slab above. In the 1 ML Ti/Al(100) surface (Model-3, $L1_2$ structure), the distances between layers 1 and 2 and layers 2 and 3 are 2.10 Å and 2.05 Å, respectively [see Table 3.2 and Fig. 3.2(c)]. The distance from a first layer Ti atom to a nearest neighbor third layer Ti atom is only 3.80 Å in this $L1_2$ slab model, which is much smaller than the Al-Al distance for the atoms belonging to the corresponding layers (4.15 Å). As a result, the surface becomes rippled upon Ti alloying.

The DFT results for pure Al(100) slabs, from 4 to 8 layers, with a $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell [see Fig. 3.2(a)], are similar to the all-electron full-potential linearized augmented plane wave results of Ref. [8]. Typically, 4- and 5-layer slabs give larger interlayer distances (by about 0.03 Å) than slabs with more layers. A fully converged pure Al slab requires at least six layers, to get reasonable values for the interlayer distances between both layers 1 and 2 and layers 2 and 3.

Our slab relaxation calculations show, however, that 4-layer Ti/Al(100) slabs give

Table 3.1: Ti binding energy ($E_{binding}^{Ti}$ in eV/Ti atom, Model-2 is taken as the energy zero), dissociation geometry, molecular chemisorption well depths (E_{well} in eV, the gas phase is taken as the energy zero), dissociation barrier heights ($E_{barrier}$ in eV), size of unit cell and functional (E_{XC}) used for H_2 molecular dissociation on pure Al(100) surface and Ti/Al(100) surfaces with different Ti coverages.

Slab Model	$E_{binding}^{Ti}$	Geometry	E_{well}	$E_{barrier}$	Unit Cell	E_{XC}
Al(100) (Model-1)	–	H2B ^a		1.03 ^g	($\sqrt{2} \times \sqrt{2}$)R45°	PW91
		H2B ^a		0.96 ^g	(2 × 2)	PW91
		H2B ^a		1.05 ^h	($3\sqrt{2} \times 3\sqrt{2}$)R45°	PBE
1/18 ML (1 st layer)	–*	Ti _{7i} 2B ^b	-0.30	-0.10 ^h	($3\sqrt{2} \times 3\sqrt{2}$)R45°	PBE
1/4 ML (1 st layer)	1.20	Ti _{7i} 2B ^b	-0.50	-0.10 ^g	(2 × 2)	PW91
		Ti _{7i} 2B ^b		0.26 ⁱ	($2\sqrt{2} \times 2\sqrt{2}$)R45°	RPBE
1/4 ML (1 st layer reconstructed)	0.88	Ti _{7i} 2H ^c	-0.52	-0.07 ^g	($2\sqrt{2} \times 2\sqrt{2}$)R45°	PW91
		B _{Al} 2H ^d		1.32 ^g	($2\sqrt{2} \times 2\sqrt{2}$)R45°	PW91
		B _{Al} 2H ^d		0.0 ⁱ	($2\sqrt{2} \times 2\sqrt{2}$)R45°	RPBE
1/2 ML (1 st layer)	0.87	Ti _{7i} 2B ^b	-0.41	0.28 ^g	(2 × 2)	PW91
		Ti _{7i} 2B ^b		1.62 ⁱ	($2\sqrt{2} \times 2\sqrt{2}$)R45°	RPBE
1/2 ML (Model-2)	0	B2T ^e		0.63 ^g	($\sqrt{2} \times \sqrt{2}$)R45°	PW91
1ML (Model-3)	0.23	–		> 1.62 ⁱ	($2\sqrt{2} \times 2\sqrt{2}$)R45°	RPBE
		Ti _{7i} 2B ^b	-0.45	0.14 ^g	($\sqrt{2} \times \sqrt{2}$)R45°	PW91
		Ti _{7i} 2B ^b	-0.45	0.23 ^g	(2 × 2)	PW91
1ML (1 st layer)	1.47	Ti _{7i} 2B ^b	-0.30	0.45 ^g	(2 × 2)	RPBE
		Ti _{7i} 2B ^f	-0.53	-0.20 ^g	(2 × 2)	PW91

* There is no comparable data available and the absolute value is -5.57 eV/Ti atom [3].

^a H₂ dissociation from Al hollow site to Al-Al bridge sites.

^b From Ti top site to Ti-Al bridge sites.

^c From Ti top site to Ti-Al-Al hollow sites.

^d From Al-Al bridge site to Ti-Al-Al hollow sites.

^e From Al-Al bridge site to Al top sites.

^f From Ti top site to Ti-Ti bridge sites.

^g Present work.

^h Ref. [3].

ⁱ Ref. [5].

Table 3.2: Interlayer distance values* (d_{12} , d_{23} and d_{34} in Å) obtained after relaxation of the 4-layer slab models investigated in the present work: Al(100) (Model-1), 1/2 ML Ti/Al(100) with Ti in the second layer (Model-2), and 1 ML Ti/Al(100) with Ti in the first and third layers (Model-3).

	d_{12}	d_{23}	d_{34}
Al(100) (Model-1)	2.076	2.051	2.076
1/2 ML (Model-2)	2.027	2.017	2.125
1ML (Model-3)	2.105	2.055	2.002

* Note that the interlayer distance values correspond to the plots in Fig. 3.2.

interlayer distances between layers 1 and 2 and between layers 2 and 3 that are accurate enough compared to the results of 5-, 6-, 7- and 8-layer slabs for both 1/2 ML and 1 ML coverages. Differences between distances of layer 1 and 2 for the slabs in Fig. 3.2(b-c) are within 0.01 Å. The Ti binding energy differences are within 0.1 eV/Ti atom. Also for reasons of computational efficiency, we therefore decided to use 4-layer slabs for obtaining H₂ dissociation barriers in the next step.

3.3.2 H₂ dissociation barriers

As pointed out in the previous subsection, Model-2 and Model-3 are the most energetically favorable structure for incorporation of Ti at 1/2 and 1 ML coverages. For these models and for the pure Al(100) slab (Model-1), mainly three 4-layer slab models have been used to study H₂ dissociation in this subsection.

Using $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface unit cells, ANEB calculations show that the barrier height for H₂ dissociating on Ti/Al(100) surfaces is dramatically influenced by the presence of Ti. For Model-1, H₂ dissociation on a pure Al(100) surface, the lowest energy barrier height is 1.03 eV (Table 3.1), with H₂ dissociating at the hollow site and the final dissociated geometry being two hydrogen atoms that occupy two neighboring bridge sites. Initial and final configurations obtained with the $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell are shown in Fig. 3.3(a), along with the reaction path for this model. The reaction coordinate is defined by

$$S_i = \sum_0^i \sqrt{(r_i - r_{i-1})^2 + (Z_i - Z_{i-1})^2}, \quad (3.8)$$

where r is the H-H distance, r_0 is the initial H₂ distance in the gas phase (0.755 Å), and Z is the distance from the H₂ COM to the surface, with an initial value of $Z_0 = 4.0$ Å. We find that the barrier is located at $r = 1.03$ Å and $Z = 1.17$ Å.

In contrast, the minimum barrier height for Model-2 is only 0.63 eV, with H₂ dis-

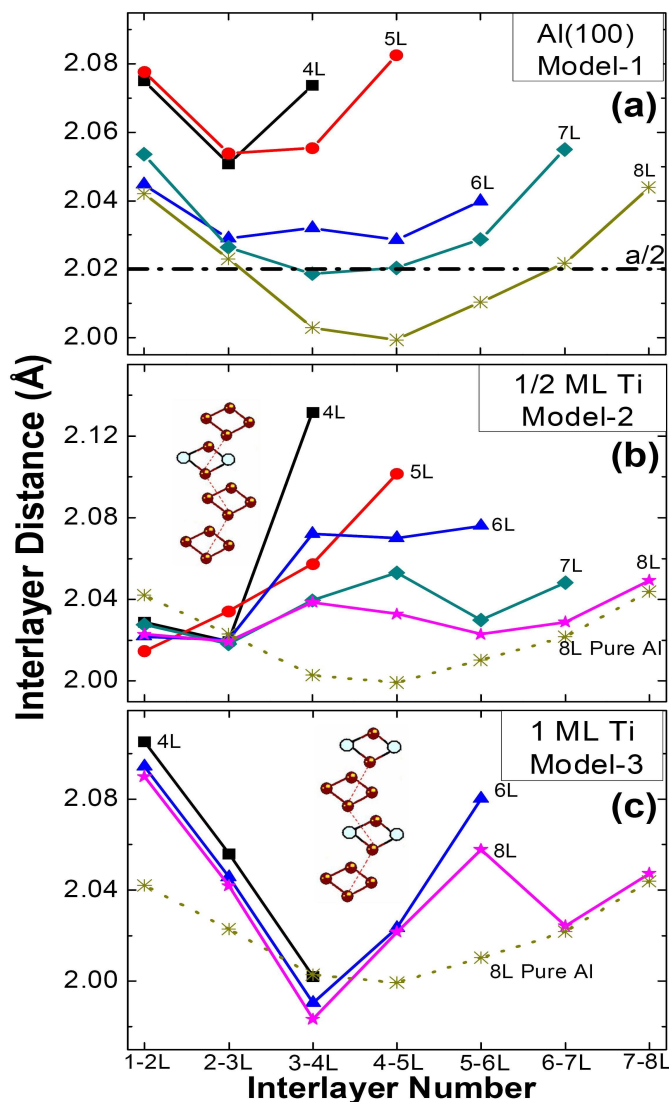


Figure 3.2: Interlayer distances for 4- to 8-layer slabs. (a) pure Al(100) slabs, in which the horizontal line marked as $a/2$ is the bulk interlayer distance. (b) Interlayer distances for 1/2 ML Ti/Al(100) surface obtained from the positions of the Al atoms connected by dashed lines in the slab model. The interlayer distances of the 8-layer pure Al slab are given by the asterisks connected by the dotted line to guide the eye; (c) same as (b) for 1 ML Ti/Al(100) surfaces. The brown and light blue spheres represent Al and Ti atoms, respectively.

sociating from bridge to top sites, as shown in Table 3.1 and Fig. 3.3(a). The barrier now appears at $r = 1.11$ Å and $Z = 1.53$ Å. The reactions for both Model-1 and Model-2 are endothermic processes, with dissociative chemisorption energies of 0.34 eV and 0.30 eV

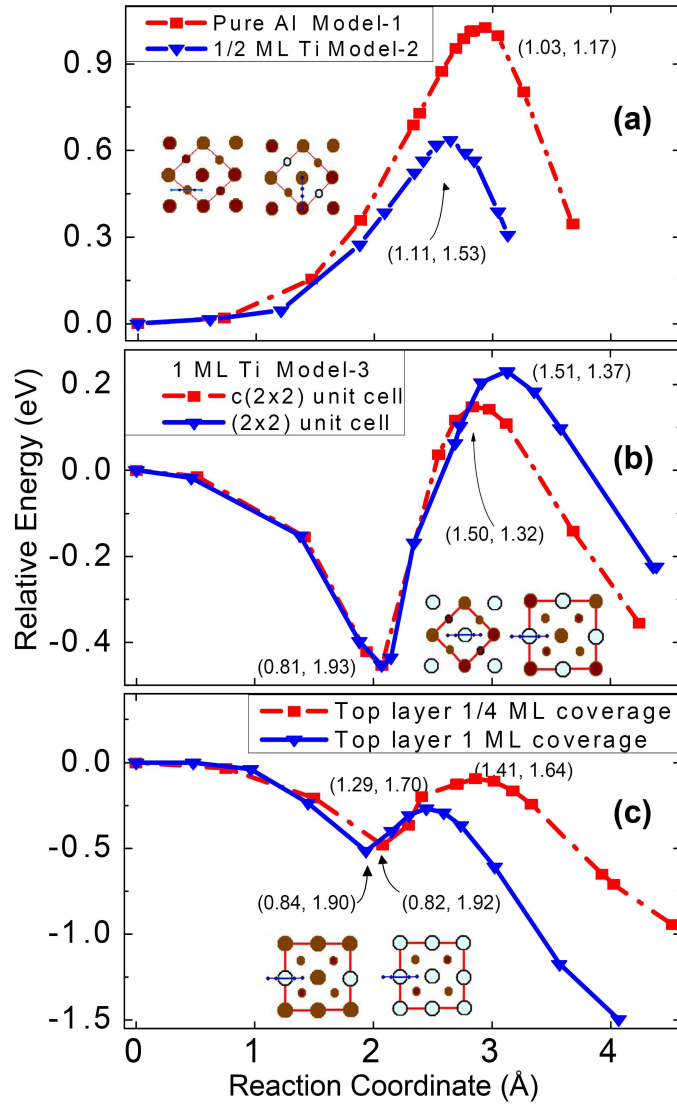


Figure 3.3: Reaction paths for H_2 dissociation, unit cells, (r, Z) for the barriers and wells are given respectively, with distance units in Å. Large (small) brown and light blue spheres represent Al and Ti atoms, respectively, in the first (second) layer. Initial and final H-H configurations are indicated by small dark blue spheres for the atoms. (a) Model-1 and Model-2 results obtained with $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cells; (b) Model-3 results obtained with $(\sqrt{2} \times \sqrt{2})R45^\circ$ and (2×2) unit cells; (c) 1/4 ML and 1 ML coverage results, obtained with Ti in the first layer employing (2×2) unit cells.

per H_2 molecule, respectively.

Model-3 seems to be the energetically most favorable model for H_2 dissociation. It

has a low barrier of 0.14 eV [see Table 3.1 and Fig. 3.3(b)], with H_2 dissociating from top Ti to bridge sites. There is a deep molecular chemisorption well, with a depth of 0.45 eV in front of the dissociation barrier, in Fig. 3.3(b). At the bottom of the well, $r = 0.81 \text{ \AA}$ and $Z = 1.93 \text{ \AA}$. The barrier is quite late, with $r = 1.50 \text{ \AA}$ and $Z = 1.32 \text{ \AA}$.

The above results show that adding a 1/2 ML Ti coverage to Al(100) could lower the barrier by about 0.40 eV, and adding 1 ML Ti coverage could lower it by 0.90 eV. It should be pointed out that the deep molecular chemisorption potential well in Model-3 appears only if H_2 dissociates above a surface Ti atom. No molecular chemisorption well appears in Model-1, Model-2 or other investigated higher barrier reaction paths of Model-3.

The heights of the barriers were further tested on 6-layer slabs, and using larger (2×2) unit cells. We find that H_2 dissociation barriers are not much influenced by the number of layers, 4-layer slabs are good enough for all three models. Using a (2×2) unit cell, the barrier height for Model-1 is 0.96 eV [1.03 eV on $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ unit cell, see also Table 3.1], which is in reasonable agreement with the PBE result of 1.05 eV using a $(3\sqrt{2} \times 3\sqrt{2})\text{R}45^\circ$ unit cell [3]. Model-3 needs a larger unit cell to avoid the lateral interaction between dissociated H_2 and its periodically repeated images due to the late barrier ($r = 1.50 \text{ \AA}$ at the barrier position). With a larger (2×2) unit cell [see Table 3.1 and Fig. 3.3(b)], the minimum barrier is 0.23 eV, 0.09 eV higher than that obtained using the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ unit cell, with $r = 1.51 \text{ \AA}$ and $Z = 1.37 \text{ \AA}$ for the larger unit cell. With Model-3 dissociative chemisorption is an exothermic process (-0.22 eV) when using the (2×2) unit cell. Because the barrier is earlier in Model-2, and because of the small H-H distance in the molecular chemisorption well of Model-3, the corresponding barrier height and the well depth are not much influenced by the size of the unit cell, the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ unit cell giving converged results. For Model-3, the RPBE functional gives a shallower well (-0.30 eV) and a higher barrier (0.45 eV) than the PW91 functional (Table 3.1).

H_2 dissociation on the slab modelling 1/2 ML Ti/Al(100) surface with Ti in the top layer [Fig. 3.1(b)], is similar to that in Model-3, except that the chemisorption well is slightly shallower and the barrier height is slightly higher (see Table 3.1). From the viewpoint of stability, this slab has a higher binding energy [Table 3.1 and Fig. 3.1(b)], by 0.64 eV/Ti atom, than Model-3. A previous study [5] suggested that H_2 dissociation on this surface [Fig. 3.1(b)] has an extremely high barrier (1.62 eV, see Table 3.1), which is at odds with our results and with the experimental finding [29] that the TiAl_3 crystal does have a catalytic effect on the reversible dehydrogenation.

Moreover, we have also investigated the case of low Ti coverage, 1/4 ML with Ti in the top layer [Fig. 3.3(c)], employing a (2×2) surface unit cell. It is found that in this case the Ti binding energy is 1.0 eV/Ti atom higher (more unfavorable) than that in Model-3 (Table 3.1). An ANEB barrier search shows, for H_2 dissociation on Ti top site, a molecular

chemisorption well with a depth of 0.50 eV and a barrier with a height of -0.10 eV relative to the gas phase H_2 energy in the reaction path [see Table 3.1 and Fig. 3.3(c)]. The H_2 dissociation is exothermic, with a dissociative chemisorption energy of -0.94 eV per H_2 molecule. A similar, low coverage study has been conducted for "isolated" Ti, in a 1/18 ML Ti/Al(100) surface with Ti in the top layer, employing a $(3\sqrt{2} \times 3\sqrt{2})R45^\circ$ unit cell [3]. On this surface, the molecular chemisorption well has a depth of 0.30 eV and the barrier height is also -0.10 eV. Thus, for H_2 dissociation, the results of the 1/18 ML Ti/Al(100) surface [3], are in good agreement with our results for the 1/4 ML Ti/Al(100) surface. Because the PBE functional was designed to reproduce PW91 energies, this suggests that the results for 1/4 ML coverage are already representative of isolated Ti in the study of 1/18 ML surface.

Another 1/4 ML Ti/Al(100) surface studied by Muckerman and coworkers [5, 6], which used a $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ unit cell with a reconstructed structure in the first layer, exhibited spontaneous H_2 dissociation over an Al-Al bridge to Ti-Al-Al hollow sites. In our calculations, the reconstructed slab is more stable than that without reconstruction by 0.32 eV/Ti atom (Table 3.1). However, for this dissociation geometry we find a barrier with height 1.32 eV, when applying the ANEB barrier search method with the same setting of the initial and final geometries as in Refs. [5, 6]. This barrier occurs at $r = 0.96 \text{ \AA}$ and $Z = 1.83 \text{ \AA}$ in our calculations. We find that H_2 dissociates with a lower barrier on this reconstructed surface in another dissociation geometry, i.e., above a top Ti site to Ti-Al-Al hollow sites, with a similar shape of the path as found for the 1/4 ML coverage surface without reconstruction (see Table 3.1).

Although the 1/4 ML Ti/Al(100) surface described above promotes dissociation very efficiently, a problem already noted is that the nearest neighbor Ti-Ti distances for this coverage and model do not correspond well with Ti-Ti distances found in EXAFS experiments, i.e., 3.80 Å on hydrogenated and dehydrogenated $NaAlH_4$ [5]. Our model of 1 ML coverage with $c(2 \times 2)$ structure (Model-3) does have a Ti-Ti nearest neighbor distance 3.80 Å, which is in excellent agreement with the EXAFS experimental results, and only exhibits modest dissociation barriers. Furthermore, the structure calculated for this higher coverage corresponds well with the structure determined experimentally for deposition of Ti on Al(100) [9, 10]. Therefore, in view of the existing experimental information, and also of the Ti binding energies, this higher coverage model appears to be the most realistic one for modelling H_2 dissociation on Ti/Al(100) surface.

Interestingly, we find that the surface with 1/4 ML of Ti in the top layer has a similar behavior to the surface that is fully covered by 1 ML of Ti in the top layer [Fig. 3.3(c)]. The latter surface has an even more positive Ti binding energy (by 1.24 eV/Ti atom compared to Model-3, see Table 3.1), which indicates that this surface is even more unstable. For this case, our ANEB results also show a molecular chemisorption well, followed by a barrier of -0.20 eV [see Table 3.1 and Fig. 3.3(c)]. On this fully Ti covered surface, the dissociative chemisorption energy is -0.94 eV per H_2 molecule.

The high Ti binding energies indicate that the following surfaces have little chance to exist in nature: (1) the 1/18 ML Ti/Al(100) surface, (2) the regular 1/4 ML Ti/Al(100) surface and the reconstructed one, (3) the 1/2 ML Ti/Al(100) surface with Ti in the first layer, and (4) the 1 ML Ti/Al(100) surface with the first layer consisting of only Ti. Ti atoms prefer to be in the second layer of the surface at low Ti coverage, or in the first and third layers with a $c(2 \times 2)$ pattern at 1 ML coverage.

In specifying the heights of the barriers to dissociation for the systems investigated above, we have consistently referenced the barrier heights to the energy of H_2 in the gas phase. In some of the models studied above, there is also a molecular chemisorption well, which precedes the barrier to dissociation. In such a case the system may be characterized by three different barriers, i.e, the barrier to dissociation referenced to the gas phase, the barrier to dissociation referenced to the molecular chemisorption well, and the barrier to molecular desorption referenced to the molecular chemisorption well [30].

The importance of these barriers has been considered in a kinetics study of an analogous model for H_2 dissociation on Ni(100) [30]. The outcome of the study was that at sufficiently high temperatures the reaction is direct and only the barrier to dissociation referenced to the gas phase is important. At low temperatures the reaction proceeds through an adsorbed intermediate, which may be thought of as a stable chemical species. In this case, the barrier that is most relevant to the kinetics is the barrier to dissociation referenced to the molecular chemisorption well. At intermediate temperatures, all barriers become important to the overall kinetics of the dissociation reaction. Processes which can contribute to sticking or trapping of H_2 in the molecular chemisorption well (either as a stable chemical species, or as a transient) are energy transfer from translation to rotation (also called rotation-mediated selective adsorption [31]), energy transfer to motion of H_2 parallel to the surface (corrugation mediated selective adsorption [32]), energy transfer to phonons, and energy transfer to electron-hole pair excitations [33]. Additional kinetics or dynamics calculations are needed to determine to what extent these processes may contribute to sticking or trapping of H_2 at the temperatures (50-150 °C) relevant to uptake and release of hydrogen by $NaAlH_4$. We hope to present results of such calculations in a follow-up paper, but note that the two additional barriers required are simply equal to the chemisorption well depth (for desorption) and to the chemisorption well depth plus the barrier for dissociation referenced to the gas phase (for dissociation of the molecule trapped at the bottom of the molecular chemisorption well). These data are all collected in Table 3.1.

In summary, Model-3 would seem to be the most realistic model for describing H_2 dissociation on Ti-covered Al(100) surfaces, from the viewpoints of both experimental information and theoretical calculations. This model has a relatively low barrier height H_2 dissociation (0.23 eV) and a deep molecular chemisorption well (-0.45 eV) in front of the dissociation barrier.

3.3.3 A molecular orbital view of the H₂ approach to the surface and the subsequent dissociation

In Fig. 3.4 the two-center PDOS of the H₂ bonding σ_g and antibonding σ_u molecular orbitals (Eqs. 3.3 through 3.6) are shown for five configurations along the H₂ reaction path of Model-3 [Fig. 3.1(c) and Fig. 3.3(b)].

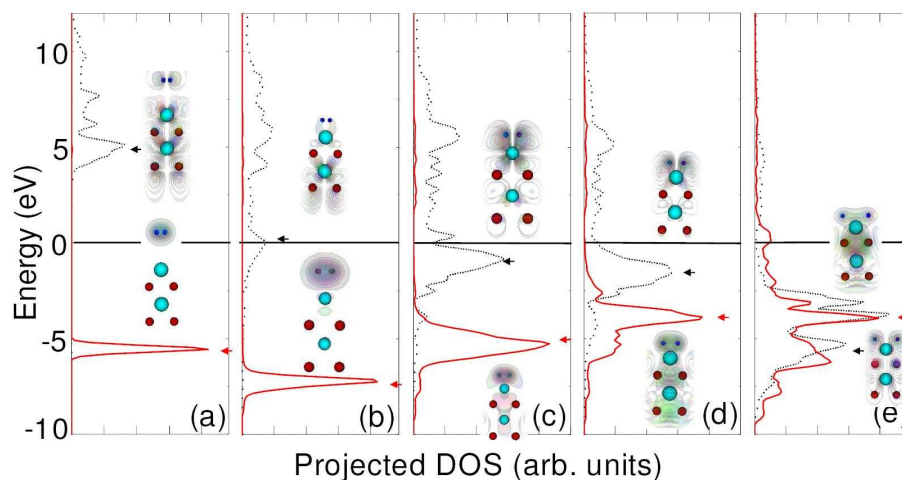


Figure 3.4: For Model-3, two-center PDOS are shown for the H-H bonding σ_g (solid red line) and the antibonding σ_u orbital (dotted black line). The Fermi level is set as the energy zero. Wavefunction plots correspond to the most intensive peaks of H-H bonding (red arrows) and antibonding (black arrows) states. Five positions are given respectively as (r, Z) , with units in Å: (a) gas phase (0.755, 4.0), (b) chemisorption well (0.81, 1.93), (c) (1.20, 1.66), (d) barrier (1.50, 1.32) and (e) (2.87, 1.31).

If the H₂ molecule is far from the surface [Fig. 3.4(a)] only the H₂ σ_g bonding state is occupied. It is essentially a molecular state that is slightly broadened due to the interaction with the surface (a part of the broadening seen in Fig. 3.4(a) is due to the finite width used to represent the δ function in Eq. 3.3). Upon H₂ adsorption in the molecular chemisorption well [Fig. 3.4(b)], the bonding state shifts to a lower energy. As can be seen from the plot of the potential energy along the reaction path shown in Fig. 3.3(b), the H₂ molecule can approach the potential well without having to overcome a barrier. The plot of the wave functions show that one of the metal orbitals involved in this process is the Ti $3d_{z^2}$ orbital. This orbital is initially nearly empty [34] and the occupied-virtual attraction between the H₂ σ_g and Ti $3d_{z^2}$ facilitates a barrier-less approach to the molecular chemisorption well. This part of the process is accompanied by a (small) transfer of charge from the H₂ molecule to the metal surface. Simultaneously we see that the H₂ σ_u orbital is broadened considerably due to the interaction with the Ti $3d_{xz}$ orbital and becomes partly occupied. This occupied-virtual attraction leads to a slight weakening of

the H_2 bond (the bond is 0.05 Å longer than in the gas phase) and a small charge transfer from the metal surface to the molecule. But the combined effect of the ($H_2 \sigma_g$ - $Ti 3d_{z^2}$) and ($H_2 \sigma_u$ - $Ti 3d_{xz}$) interactions results in no net transfer of charge between the molecule and the metal surface.

Moving further along the reaction path we see that the $H_2 \sigma_g$ bonding state shifts to higher energies again [Fig. 3.4(c) through Fig. 3.4(e)]. This is due to a reduction in overlap between the $H_2 \sigma_g$ and $Ti 3d_{z^2}$ orbitals. At the same time the overlap between the $H_2 \sigma_u$ and $Ti 3d_{xz}$ orbitals increases, leading to a further lowering of the energy of the $H_2 \sigma_u$ antibonding state, accompanied by an increasing occupation. Apparently the reduction in overlap between $H_2 \sigma_g$ and $Ti 3d_{z^2}$ is initially faster than the gain in overlap between $H_2 \sigma_u$ and $Ti 3d_{xz}$, thereby giving rise to an increasing potential energy moving from Fig. 3.4(b) to Fig. 3.4(c) to Fig. 3.4(d). Towards the end of the reaction path (i.e., after the barrier) the trend is reversed and the increase in overlap between $H_2 \sigma_u$ and $Ti 3d_{xz}$ “wins” over the decrease in overlap between $H_2 \sigma_g$ and $Ti 3d_{z^2}$, giving rise to a stable, dissociated state of low energy.

From the analysis of the two-center PDOS, the catalytic role played by Ti for H_2 dissociation is that the transition metal atom can provide a $3d_{z^2}$ orbital and a $3d_{xz}$ orbital simultaneously, which helps to dissociate H_2 . The absence of such orbitals in pure Al or NaH explains why H_2 dissociation on these surfaces is not a favorable process.

To understand the interaction of H_2 with the Ti/Al(100) surface alloy, it is illuminating to consider the case of H_2 interacting with another alloy surface involving Al, i.e., NiAl(110). In the NiAl(110) surface system [25], the d orbitals of the Ni atom are fully filled. The dissociation of H_2 on this surface is likewise dominated by a local chemical behavior due to the ($H_2 \sigma_g$ - $Ni 3d_{z^2}$) and ($H_2 \sigma_u$ - $Ni 3d_{xz}$) interactions [25]. Thus, it cannot be described in terms of the Harris-Andersson model [35], in which the empty $3d$ bands of the transition metal serve initially as sinks for $4s$ electrons of the transition metal and reduce the Pauli repulsion, and thereby lower the molecular dissociation barrier. The main difference of Ti/Al(100) with NiAl(110) comes from the almost empty $3d_{z^2}$ orbital in Ti, which makes for a barrier-less approach to a deep molecular chemisorption well in Ti/Al(100). In contrast, H_2 dissociation on NiAl(110) takes place without molecular chemisorption and is highly activated, because the $Ni 3d_{z^2}$ orbital is full. Note that, upon rotation of H_2 over 90° , the ($H_2 \sigma_u$ - $Ti 3d_{yz}$) interaction can play the same role as the ($H_2 \sigma_u$ - $Ti 3d_{xz}$) interaction, because of the C_{4v} symmetry on the $c(2 \times 2)$ -Ti/Al(100) surface.

3.4 Conclusions

We have used density functional theory with the PW91 functional to model Ti/Al(100) alloy surfaces and dissociation of H₂ on these surfaces, with a view to understanding the catalytic role of Ti and hydrogen release from and uptake in NaAlH₄. Ti/Al(100) surfaces were investigated with Ti coverages varying from 1/4 to 1 ML, with emphasis on c(2 × 2) structures modeling 1/2 and 1 ML coverages.

At 1/2 ML coverage, the energetically preferred c(2 × 2) structure (Model-2), with the lowest energy of Ti per Ti atom in Al, has the Ti atoms present in the second layer. At 1 ML coverage, the energetically preferred structure (Model-3), has the Ti atoms present in the first and third layers, again in a c(2 × 2) structure, with the Ti atoms in the third layer being underneath the Ti atoms in the first layer. In Model-2, the presence of Ti lowers the barrier for H₂ dissociation from 0.96 eV for a pure Al(100) surface (Model-1) to 0.63 eV. In Model-3, the presence of Ti lowers the barrier for H₂ dissociation even further, to only 0.23 eV, whereas the binding energy of Ti is higher by 0.23 eV/Ti atom than that in Model-2. Models with 1 ML and 1/4 ML coverages, with the Ti atoms present only in the first layer, have been found to exhibit even lower barriers to H₂ dissociation, but these show much higher binding energies for Ti in Al(100) slabs, and the Ti-Ti distances in these structures are in disagreement with the values obtained in EXAFS experiments. Because the Ti-Ti distance obtained with Model-3 is in excellent agreement with these experiments, and because Model-3 only exhibits a low barrier to H₂ dissociation, we conclude that this model represents the best model for describing Ti-catalyzed H₂ dissociation on Al(100) surfaces. With Model-3, H₂ dissociation is exothermic, and in the reaction path there is a molecular chemisorption well of depth 0.45 eV between the gas phase and the reaction barrier.

The two-center projected density of states analysis provides a molecular orbital view in which the barrier-less approach to the molecular chemisorption well occurring in Model-3 is mainly explained by an occupied-virtual attraction between the H₂ σ_g and Ti 3d_{z²} orbitals. The barrier separating the molecular chemisorption well and the dissociated state can be understood as resulting from a competition between increasing overlap of the H₂ σ_u and Ti 3d_{xz} orbitals, and decreasing overlap of the H₂ σ_g and Ti 3d_{z²} orbitals.

This chapter suggests that, to promote H₂ dissociation, the amount of Ti added should be high enough to provide, at least locally, a c(2 × 2)-Ti/Al(100) surface alloy with a Ti coverage of 1 ML, where Ti atoms are present in both the first and the third layer of the alloy surface.

3.5 References

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Chapter 4

Six-dimensional quasi-classical and quantum dynamics for H₂ dissociation on the 1 monolayer covered c(2 × 2)-Ti/Al(100) surface

This chapter is based on:

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Abstract

Based on a slab model of H₂ dissociation on a c(2 × 2) structure with Ti atoms in the first and third layers of Al(100), a six-dimensional (6D) potential energy surface (PES) has been built. In this PES, a molecular adsorption well with depth of 0.45 eV is present in front of a barrier of height 0.13 eV. Using this PES, H₂ dissociation probabilities are calculated by the classical trajectory (CT), the quasi-classical trajectory (QCT) and the time-dependent wave-packet (TDWP) method. The QCT study shows that trajectories can be trapped by the molecular adsorption well. Higher incident energy can lead to direct H₂ dissociation. Vibrational pre-excitation is the most efficient way to promote direct dissociation (without trapping). We find that both rotational and vibrational excitation have efficacies close to 1.0 in the entire range of incident energies investigated, which supports the randomization in the initial conditions making the reaction rate solely depend on the total (internal plus translational) energy. The H₂ dissociation probabilities from quantum dynamics are in reasonable agreement with the QCT results in the energy range 50 – 200 meV, except for some fluctuations. However, the TDWP results considerably exceed the QCT results in the energy range 200 – 850 meV. The CT reaction probabilities are too low compared with the quantum dynamical results.

4.1 Introduction

Plausible explanations of the elementary reaction steps and the corresponding reaction dynamics are key to understanding the complex chemical reactions in hydrogen storage materials, e.g. sodium alanate ($NaAlH_4$) [1]. In a previous study of H_2 reacting on Ti/Al(100) surfaces [2], it was found that the most realistic model promoting H_2 dissociation is a 1 monolayer (ML) Ti covered $c(2 \times 2)$ -Ti/Al(100) structure, with Ti atoms in the first and third layers. This model has a minimum energy path (MEP) with a late barrier of only 0.13 eV height at an H–H distance of 1.50 Å, and a deep molecular adsorption well with a depth of 0.45 eV in front of the barrier at an H–H distance of 0.82 Å. Such a molecular adsorption well could lead to sticking and/or trapping of the H_2 molecules on the Ti/Al(100) surface. Processes which can contribute to trapping of H_2 in the molecular adsorption well are energy transfer from translation to rotation (also called rotation-mediated selective adsorption [3]), energy transfer to motion of H_2 parallel to the surface (corrugation mediated selective adsorption [4]), energy transfer to phonons, and energy transfer to electron-hole pair excitations [5]. In order to determine to what extent these processes may contribute to sticking of H_2 at the temperatures (50–150 °C) relevant to uptake and release of hydrogen by $NaAlH_4$, reaction probabilities from (quasi-) classical or quantum dynamics are needed. The aim of the present work is to investigate the dynamics of the $H_2 + Ti/Al(100)$ reaction from this point of view.

For the analogous $H_2 + Ni(100)$ reaction, which has a shallow molecular adsorption well with a depth of 0.13 eV [6], it is justified to treat the dissociation dynamics as a direct process and ignore the molecular adsorption at sufficiently high surface temperatures. Therefore, at high surface temperature only the barrier to dissociation referenced to the gas phase is important. However, at low surface temperature the reaction proceeds through a molecularly adsorbed intermediate, which may be thought of as a stable chemical species. In the latter case, the barrier relevant to the kinetics is the barrier to dissociation referenced to the molecular adsorption well. Reactions proceeding over deep potential energy wells can be treated statistically, if the intermediates are sufficiently long lived [7]. In this case, a treatment of the formation and decay of the intermediates into reactant and product channels may be enough to give satisfactory results [8, 9].

Increasing interest in the role of rotational and vibrational energy in promoting molecule-surface reactivity is driven by the development of new theoretical methods and experimental tools allowing a more insight into the details of a reaction [10, 11]. One of the widely studied systems, H_2 (D_2) + Cu(111) [12–19] is a late barrier system like the system under investigation here. H_2 (D_2) shows a preference for reaction in the helicopter approach (a positive rotational quadrupole alignment parameter) [19–21] to the Cu(111) surface, which indicates there is a steric effect in the dynamics. Both experimental [16, 17] and theoretical [19] studies show this system has rotational and vibrational efficacies of 0.40 and 0.65, respectively. Thus, the statistical model [22] with a random-

ization of the initial conditions can not be applied to this direct reaction. One question addressed here is whether the same conclusion can be drawn for the late barrier system $H_2 + \text{Ti/Al(100)}$, which has a deep molecular adsorption well in front of the barrier.

The Born-Oppenheimer (BO) approximation has been found to accurately describe the dissociation of H_2 on metal surfaces [23], because H_2 has a low electron affinity and the net charge transfer is almost zero during the process of dissociation [2, 23, 24]. Thus, we neglect electron-hole pair excitation. Due to the mismatch between the mass of H_2 and surface Ti and Al atoms, the energy transfer from the molecule to the metal surface should be small and unlikely to influence the scattering result. Therefore, the Ti/Al(100) slab can be fixed during the process of H_2 dissociation, and we only consider the motion in the six degrees of freedom (DOFs) on the ground state PES.

Theoretical progress in gas-surface reaction dynamics [11, 25–31] combined with super computer facilities [32] make six-dimensional quantum dynamics calculations of H_2 –surface reaction dynamics possible. Six-dimensional quantum dynamics has been successfully implemented to address the dissociative chemisorption of H_2 on Pd(100) [25, 33], Pd(110) [34], Rh(100) [33], Cu(100) [30, 35], Cu(111) [18, 19, 26, 28], Pt(111) [23, 36], Pt(211) [37], Pd(111) [38], Ru(0001) [39], NiAl(110) [40], and on sulfur-precovered Pd(100) [41] and CO-precovered Ru(0001) [42].

Based on a slab model of the 1 ML Ti covered Ti/Al(100) surface [2], a 6D PES has been built by density functional theory (DFT) [43, 44]. Both the quantum and quasi-classical dynamics are calculated on it. Our results show that the H_2 dissociation probabilities obtained from quantum dynamics and quasi-classical dynamics agree well with each other in the low incident energy range, except that the quantum probability has many peaks (associated with the opening up of new rovibrational states or resonances). However, the quantum probability is higher than the quasi-classical one up to 30.0 % at incident energies above 0.30 eV.

The layout of this chapter is as follows. The methodology and numerical details are presented in Section 4.2, in which Section 4.2.1 describes electronic structure calculations by DFT, Section 4.2.2 describes the building of the 6D PES, Section 4.2.3 describes the CT and QCT calculations, and Section 4.2.4 describes the TDWP calculations. Results are presented and discussed in Section 4.3. Specifically, Section 4.3.1 shows the location of the data points and cuts through the PES. Section 4.3.2 focuses on the H_2 dissociation probability calculated by QCT. In Section 4.3.3, comparisons of the CT, QCT and TDWP results are presented. Finally, conclusions and an outlook are presented in Section 4.4.

4.2 Methodology and numerical details

4.2.1 Electronic structure calculations and slab model

The DFT code DACAPO [45] is used to study H_2 dissociation on the 1 ML $c(2 \times 2)$ - Ti/Al(100) slab model with Ti atoms in the first and third layers. The PW91 functional [46], which has been shown to give reasonably good results for H_2 dissociating on the NiAl(110) alloy surface [40, 47], is employed to describe the exchange-correlation energy of the electrons. The ion cores are described by ultrasoft pseudopotentials [48], with core cutoff radii of $r_c^H = 0.46 \text{ \AA}$, $r_c^{Al} = 0.84 \text{ \AA}$ and $r_c^{Ti} = 1.16 \text{ \AA}$. A plane wave basis set is used for the electronic orbitals, with a cutoff energy of 350 eV. The Brillouin zone is sampled by the Monkhorst-Pack [49] method, using a set of $6 \times 6 \times 1$ k -points. In the Z direction (perpendicular to the surface, see Fig. 4.1), a vacuum layer of 12.0 $\text{\AA}$ was placed between the slabs to avoid artificial interactions caused by the periodic boundary conditions. The lattice constant of the surface unit cell is $a = 4.04 \text{ \AA}$, and more details of the slab structure can be found in Chapter 3.

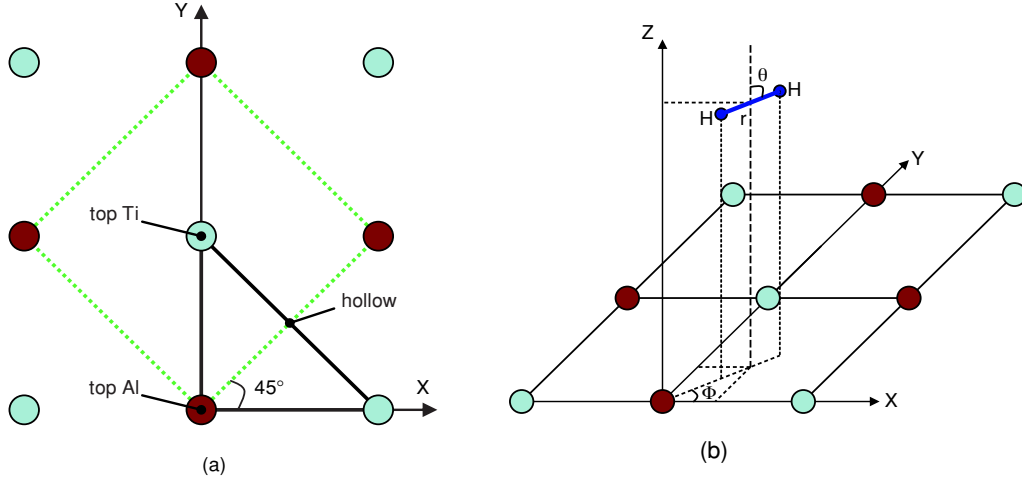


Figure 4.1: (a) (2×2) surface unit cell of Ti/Al(100) with lattice constant $a = 4.04 \text{ \AA}$. The brown and blue spheres represent Al and Ti atoms, respectively. The isosceles right triangle (including three boundaries) in black color formed by two Ti atoms and one Al atom, is the area used for adding Grow data points and for the implementation of the quasi-classical simulation. Once the process of adding points to the data set is finished, the potential is set up on the $(\sqrt{2} \times \sqrt{2})$ unit cell (dotted green square area) by using symmetric operations. (b) The coordinates used for H_2 + Ti/Al(100): the H-H atomic distance r , the position of the H_2 COM over the alloy surface (X, Y, Z) , the polar angle θ , and the azimuthal angle ϕ .

A three-layer Ti/Al(100) slab model is employed in this work to study the H_2 dis-

sociation dynamics (see Fig. 4.1). Using a (2×2) unit cell, although the interlayer distance between the first-layer Ti and the third-layer Ti is compressed from 3.80 Å in the four-layer model to 3.67 Å in the three-layer model after relaxation, our convergence tests show that the H_2 geometries in the molecular adsorption well and at the barrier in this three-layer model are quite similar (difference is less than 0.05 Å) to the previous four-layer slab model results [2] using a plane wave cutoff energy of 400 eV and a $12 \times 12 \times 1$ k -point sampling. Most importantly, using this three-layer model, the depth of the molecular adsorption well and the barrier height are 0.43 eV and 0.13 eV, respectively (converged values calculated with the four-layer slab model are 0.45 eV and 0.13 eV respectively). These approximations (using less layers and k -points, and a smaller plane wave cutoff energy) save considerable CPU time in calculating the second order derivatives for the Hessian matrix, as required to build a 6D PES for the $H_2 + \text{Ti/Al(100)}$ reaction (discussed in the next Section, 4.2.2). Forward differencing with a hydrogen atomic displacement distance of 0.01 Å is used to calculate the Hessian. On the basis of tests performed with these parameters, the DFT potential energies are converged to within 5.0×10^{-2} eV.

To get accurate vibrational modes, another DFT package Vienna *ab initio* simulation program (VASP) [50–52] is used to calculate the vibrational frequency along the MEP. In these calculations, the four-layer slab model in the previous Chapter 3 is employed [2], in which a vacuum layer of 15.0 Å was placed in the Z direction. The PW91 functional and PW91 projector augmented wave (PAW) pseudopotentials [53] are used, with plane wave cutoff energy 450 eV and using an $8 \times 8 \times 1$ Monkhorst-Pack k -point sampling. Numerical centered finite differences and atomic hydrogen displacements of 0.015 Å are used to calculate the vibrational frequency, for 178 points along the MEP.

Our tests also show that the PW91 functional gives results similar to the PBE functional [54], which is expected because the PBE functional was designed to reproduce PW91 energies [54]. We also tested the RPBE functional [55] and found that it typically gives higher barriers than the PW91 functional, by about 0.25 eV. This is in accordance with recent theoretical [39] and experimental [56] works on $H_2 + \text{Ru(0001)}$, $H_2 + \text{Cu(111)}$ [18], N_2 on W(100) and W(110) surfaces [57], where the RPBE dissociation barrier heights were likewise larger than the PW91 barrier heights, and the realistic barrier heights probably fall in between the PW91 and RPBE values [18].

4.2.2 Modified Shepard interpolation method and “growing” of the six-dimensional PES

To obtain a global PES, we have used a modified Shepard (MS) interpolation procedure [58–61] initially developed by Collins and coworkers for gas phase reactions, and later adapted for studying the molecule-surface dissociative chemisorption reaction [62]. The

procedure of the application of the MS interpolation is informally known as the “Grow” method [58–61], in which the energy of the data points are obtained from the slab model mentioned above by DFT. The locations of these data points are centered on the dynamically interesting regions, *i.e.*, the most frequently visited regions by quasi-classical trajectories. The MS interpolation method is efficient and accurate enough [63, 64] compared with the corrugation reducing procedure (CRP) developed by Busnengo and coworkers [65, 66].

For 6D and higher dimensionality molecule-surface systems, MS interpolation is an efficient method to get accurate descriptions of molecule-surface interaction potential energy surfaces. Successful applications of the MS method to dissociative chemisorption of a molecule on a metal surface have been demonstrated for a number of examples, such as $N_2 + \text{Ru}(0001)$ [67, 68], $H_2 + \text{Pt}(111)$ [62], $H_2 + \text{Pd}(111)$ [69], H_2 on CO-precovered $\text{Ru}(0001)$ [42] and $\text{CH}_4 + \text{Ni}(111)$ systems [70, 71].

The PES is constructed using inverse interatomic distances $Q_i = 1/R_i$, which give a better mathematical behavior than the interatomic distances R_i when two atoms come close to each other (the singularities at $R_i \rightarrow 0$ are transformed away to $Q_i \rightarrow \infty$) [61]. For a system with N atoms, the number of interatomic distances is given by $N(N-1)/2$. Thus, in the system of $H_2 + \text{Ti/Al}(100)$, $N = 5$ atoms are required (two hydrogen and three frozen surface atoms) to represent the six H_2 DOFs, using two Ti atoms and one Al atom that form an isosceles right triangle. A configuration in the system is described using a vector of inverse inter-atomic distances, $\mathbf{Q} = \{Q_1, Q_2, \dots, Q_{N(N-1)/2}\}$. For any configuration of the system $\mathbf{Q}$, a vector of $3N - 6$ independent coordinates, $\xi(\mathbf{Q})$, can be defined in terms of the inverse interatomic distances, via a singular value decomposition [59, 61, 62]:

$$\xi_n = \sum_{k=1}^{N(N-1)/2} U_{nk} Q_k \quad (n = 1, \dots, 3N - 6). \quad (4.1)$$

According to the MS interpolation method, the potential at a given configuration $\mathbf{Q}$, in the vicinity of the data point $\mathbf{Q}(i)$, is given by a second-order Taylor expansion $T_i(\mathbf{Q})$:

$$\begin{aligned} T_i(\mathbf{Q}) = & V[\mathbf{Q}(i)] + \sum_{k=1}^{3N-6} [\xi_k - \xi_k(i)] \frac{\partial V}{\partial \xi_k} \Big|_{\mathbf{Q}=\mathbf{Q}(i)} \\ & + \frac{1}{2} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} [\xi_k - \xi_k(i)] [\xi_j - \xi_j(i)] \frac{\partial^2 V}{\partial \xi_k \partial \xi_j} \Big|_{\mathbf{Q}=\mathbf{Q}(i)}. \end{aligned} \quad (4.2)$$

The value of the potential energy at data point $\mathbf{Q}(i)$, $V[\mathbf{Q}(i)]$, and the gradients with respect to ξ at this point are calculated analytically with DFT. The second derivatives of the potential are calculated using numerical forward finite differences of the gradients, displacing the H atoms by 0.01 Å.

The MS interpolation gives the potential energy at any configuration $\mathbf{Q}$ as a weighted average of the Taylor expansion terms $T_i (i = 1, \dots, N_{data})$ calculated from each of the N_{data} data points presented in the PES data set and all symmetry equivalent points:

$$V(\mathbf{Q}) = \sum_{g \in G} \sum_{i=1}^{N_{data}} w_{g \circ i}(\mathbf{Q}) T_{g \circ i}(\mathbf{Q}). \quad (4.3)$$

In Eq. 4.3, G is the symmetry subgroup of the system and $g \circ i$ denotes the transformation of the i th data point by the group element g . The symmetry of the system is taken into account by summing over the data points in the PES data set and the symmetry equivalent points. The nuclear permutation subgroup, C_{2v} is effectively used for the $H_2 + \text{Ti/Al}(100)$ system [see the isosceles right triangle with two Ti atoms and one Al atom mentioned above in Fig. 4.1(a)], although the full symmetry should be C_{4v} . To take into account the full C_{4v} surface symmetry, the number of interatomic distances to be considered should be increased by introducing more surface atoms into the representation of PES by the Taylor expansion in Eq. 4.2, also see Fig. 4.1.

The normalized weight function $w_{g \circ i}(\mathbf{Q})$ for a given configuration $\mathbf{Q}$ depends on how close it is to another configuration $\mathbf{Q}(i)$ in the configuration space, and is defined by

$$w_{g \circ i}(\mathbf{Q}) = \frac{v_i(\mathbf{Q})}{\sum_{g \in G} \sum_{k=1}^{N_{data}} v_{g \circ k}(\mathbf{Q})}. \quad (4.4)$$

The unnormalized weight function, $v_i(\mathbf{Q})$, can have two forms. When there are few points (less than 500) in the data set, a simple one-part weight function form for $v_i(\mathbf{Q})$ is used

$$v_i(\mathbf{Q}) = \frac{1}{\|\mathbf{Q} - \mathbf{Q}(i)\|^{2p}}, \quad (4.5)$$

where we take $2p > 3N - 3$ to ensure that data points $\mathbf{Q}(i)$ far from the configuration $\mathbf{Q}$ make a negligible contribution to the interpolated energy. When there are a sufficient number of data points, a more accurate form of the unnormalized two-part weight function is employed

$$v_i(\mathbf{Q}) = \left\{ \left[\sum_{n=1}^{N(N-1)/2} \left(\frac{Q_n - Q_n(i)}{rad_n(i)} \right)^2 \right]^q + \left[\sum_{n=1}^{N(N-1)/2} \left(\frac{Q_n - Q_n(i)}{rad_n(i)} \right)^2 \right]^p \right\}^{-1}, \quad (4.6)$$

where $p = 12$ and $q = 2$. The *confidence radius* $rad_n(i)$ is defined by Bayesian analysis [61] based on an energy error tolerance (0.54 meV was used in this chapter) and a restricted set C of nearest neighbouring data points ($C = 40$ points in the present work). The benefit of the two-part weight function is that it ensures that a single Taylor expansion does not spuriously introduce sharp gradients in the PES. For example, the Taylor

expansions are not just functions of distance, they are also functions of direction. Distorting a data point geometry in one direction might correspond to compressing an already short bond, so that the quadratic Taylor expansion alone in Eq. 4.2 might not be accurate over this large distortion of the molecule. Conversely, distorting a data point geometry in another direction might correspond to a relative rotation of two distant molecular fragments, which is accurately described by the Taylor expansion [61]. The *confidence radius* in Eq. 4.6 allows these effects to be described accordingly.

An advantage of the MS interpolation method is that the sampling of data points can be performed non-uniformly over the configuration space. This can be done so that only the dynamically relevant regions of the PES will contribute significantly, through adding points in these regions to the data set. These dynamically relevant regions are found by performing QCT calculations (see below). The new data points to be added to the PES data set are selected according to the *h-weight* criterium and (or) the *variance criterium*. Using the *h-weight* criterium [58, 61], new points are added in the region most frequently visited by the trajectories, so long as there are not already too many data points representing this region in the PES data set. Different configurations N_{traj} sampled by the trajectories are stored every 50 time steps [$\Delta t = 0.01$ atomic unit (a.u.) per step]. The quantity of *h-weight* is calculated by $h(k)$ for each of these stored N_{traj} configurations,

$$h(k) = \frac{\sum_{m=1, m \neq k}^{N_{traj}} v_m[\mathbf{Q}(k)]}{\sum_{i=1}^{N_{data}} v_i[\mathbf{Q}(k)]}, \quad (4.7)$$

in which m is over all points recorded in the classical trajectories, and v_m is the unnormalized weight function in Eq. 4.6 of the difference between the recorded geometry $\mathbf{Q}(k)$ and the geometry of one of the N_{traj} points in the numerator term. The integer i runs over the points in the data set of N_{data} , in the denominator term. The value of $h(k)$ is large when $\mathbf{Q}(k)$ is both near other points visited by the trajectories and far away from the points in the data set. In the variance criterium [61], it is assumed that a new added point should be in the region where the intertrapolation by the weighted Taylor expansions is the most inaccurate, according to a weighted mean square deviation criterium,

$$\sigma^2(k) = \sum_{i=1}^{N_{data}} w_i[\mathbf{Q}(k)] \{T_i[\mathbf{Q}(k)] - V[\mathbf{Q}(k)]\}^2. \quad (4.8)$$

Here, $V[\mathbf{Q}(k)]$ is the interpolated energy in Eq. 4.3 and $T_i[\mathbf{Q}(k)]$ is the Taylor expansion value in Eq. 4.2.

If a number of data points that have significant weight $w_i[\mathbf{Q}(k)]$ lead to widely differing values of $T_i[\mathbf{Q}(k)]$ and $V[\mathbf{Q}(k)]$, the $\sigma^2(k)$ will be large and the PES may be inaccurate in the neighborhood of $\mathbf{Q}(k)$. Hence, $\mathbf{Q}(k)$ is chosen as a new data point under this criterion.

The procedure of adding new points to the data set in the Grow method follows the following steps:

- (1) Generate an initial PES data set by employing the three-layer slab model with a (2×2) unit cell, which contains 73 data points along three different reaction paths for H_2 dissociation on the Ti/Al(100) surface. The three one-dimensional reaction paths correspond to H_2 dissociation on top Ti, top Al and hollow sites. The single point potential energies are calculated by the DFT code Dacapo using the PW91 functional discussed in the previous Section 4.2.1, in which the second order derivatives are calculated with numerical forward finite differences.
- (2) Using this initial PES data set, run 20 QCTs on the interpolated PES. Trajectory configurations are recorded every 50 time steps [the time step Δt is 0.01 atomic unit (a.u.)]. From these recorded trajectory configurations, new data points are selected according to the h-weight criterium and variance criterium alternately (*i.e.*, the first data point is selected by the h-weight criterium, the next one by the variance criterium, and so on) and added to the data set.
- (3) After repeating the above two steps under point (2), until 100 new points have been added to the PES, the reaction probability for a number of initial H_2 rovibrational states and collision energies is computed by running 5000 quasi-classical trajectories for each state and collision energy. If the reaction probability is not converged, we return to step (2) above, and continue the Grow process. Otherwise, if the reaction probabilities are converged to within a standard error of 0.70 %, we stop adding new points, and the Grow process ends.

In order to have an accurate PES for the $H_2 + \text{Ti/Al(100)}$ reaction, a total number of $N_{data} = 4315$ points (4242 added points and 73 in the initial data set) are needed in the final data set. An illustration of the convergence process for two different H_2 initial states with several incident energies is shown in Fig. 4.2. In our case, reaction probabilities at low incident energies converge faster and have smaller errors than probabilities at higher incident energies. This phenomenon can be explained by the fact that convergence at higher energies requires sampling in a larger region of the PES, and that small probabilities computed with the QCT method and Monte Carlo sampling have small absolute errors in them. In the non-activated system $H_2 + \text{Pd(111)}$ [69] studied by Busnengo and coworkers, it was found that low energy trajectories can also explore large parts of the PES. In their system, 83 % of the data points are added in the exit channel even at a low incident energy of 25 meV [69], and in this aspect the $H_2 + \text{Pd(111)}$ system differs from the activated system studied here.

4.2.3 CT and QCT calculations

As already mentioned, quasi-classical trajectories were run to find and sample the dynamically relevant regions of the PES during the Grow process, and to compute reaction

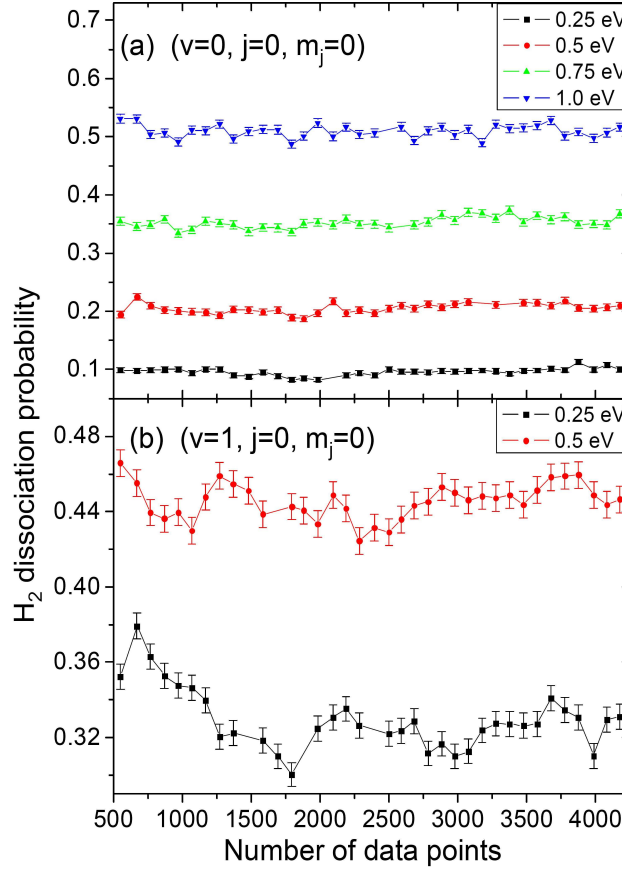


Figure 4.2: (a) Grow reaction probability convergence with error bar for the H_2 initial vibrational ground state ($v = 0, j = 0$). Results are shown for initial incident energies 0.25 eV, 0.5 eV, 0.75 eV and 1.0 eV. (b) The same as (a) but now results for the first vibrationally excited state ($v = 1, j = 0$) are shown for incident energies 0.25 and 0.50 eV. In total 4315 data points are added to the data set.

probabilities. The initial rovibrational energy of the $H_2(v, j, m_j)$ molecule is taken into account by sampling the initial condition of the trajectories from a micro-canonical ensemble. The velocities of H-atom A and B are calculated using $\mathcal{V}_A = \mathcal{V}_z + \mathcal{V}_{vib} + \mathcal{V}_{rot}$ and $\mathcal{V}_B = \mathcal{V}_z - \mathcal{V}_{vib} - \mathcal{V}_{rot}$ as described in Chapter 2.6. In the QCT calculations, the vibrational zero-point energy (ZPE) with a value of 0.27 eV is modelled in the trajectories. For the cartwheel rotationally excited state ($v = 0, j = 4, m_j = 0$) and helicopter rotationally excited state ($v = 0, j = 4, m_j = 4$), the initial energy of the trajectories also includes the rotational energy $E_{rot} = 0.14$ eV. For the first vibrationally excited state ($v = 1, j = 0$) the vibrational energy is set to $E_{vib} = 0.78$ eV. Normal incidence is modelled in all cases. In the CT calculations, the zero-point vibrational energy is not taken into account.

The initial vibrational motion of the two H atoms is taken according to a Morse

Table 4.1: The quantum states of H_2 that are sampled while adding data points to the PES data set using the Grow method at different kinetic energy E_{kin} (eV). The vibrational state is given by v , the rotational quantum number by j and the magnetic rotational quantum number by m_j .

E_{kin}	v	j	m_j
0.23	0	0	0
0.23	0	4	0
0.23	0	4	4
0.50	0	0	0
0.50	0	4	0
0.50	0	4	4
0.70	0	0	0
0.90	0	0	0
0.90	0	4	0
0.90	0	4	4
1.20	0	0	0
1.20	0	4	4
1.50	0	0	0
0.00	1	0	0
0.23	1	0	0
0.40	1	0	0
0.50	1	0	0

potential [72]. Inclusion of the ZPE in the dynamics makes an adiabatic transfer of the energy from internal vibration to translation possible, a phenomenon which is called vibrational softening. Although this may lead to ZPE violation, the QCT method usually gives more accurate results for H_2 -surface reactions than the purely classical method [11, 31].

Calculations are carried out for several different initial quantum rovibrational states (v, j, m_j) . The initial angular momentum is fixed according to $|\mathbf{L}| = \sqrt{j(j+1)}$, and the orientation of the $\mathbf{L}$ vector is selected randomly with the constraint of

$$\cos(\theta_L) = \frac{m_j}{\sqrt{j(j+1)}}, \quad (4.9)$$

where θ_L is the angle between $\mathbf{L}$ and the Z axis (which is perpendicular to the surface).

The CT and QCT simulations are implemented in an isosceles right triangle of the (2×2) unit cell formed by two Ti atoms and one shared neighboring Al atom [Fig. 4.1(a)], in which the projections of the initial configurations of the trajectories on the surface are inside the surface triangle and sampled by the Monte Carlo method. The trajectories are reflected back into the triangle when they reach the boundaries, according to the boundary

conditions [see Fig. 4.1(a)] and using the symmetry. All the initial configurations correspond to H_2 in the gas phase, with $Z = 4.0$ Å above the surface unit cell, see Fig. 4.1(b). The details of the sampling states, *i.e.*, the kinetic energy E_{kin} and the (v, j, m_j) states used to “grow” the PES are in Table 4.1. If the final H–H distance is larger than 2.64 Å, the H_2 molecule is considered to be dissociated. Otherwise, the H_2 molecule is considered to be reflected from the surface to the gas phase when its distance to the surface in Z exceeds 4.0 Å and H_2 has a velocity pointing towards the vacuum. The reaction probability in the micro-canonical ensemble is calculated as the ratio of the number of dissociated trajectories and the total number of trajectories run.

The strict localization of the system makes the CT and QCT methods easy to implement. However, quantum effects [73] which should be important for H_2 , are not considered yet, which is the reason that we also need to calculate the H_2 dissociation probabilities by the quantum wave packet method in the next subsection to test the accuracy of the QCT and CT methods. Because of the deep molecular adsorption well in the PES, quantum effects, such as resonances or tunneling, can be especially important for the reaction dynamics.

4.2.4 TDWP calculations

In the quantum dynamics, the six H_2 coordinates used are the hydrogen inter-molecular distance r , its center of mass coordinates (X, Y, Z) , the polar angle of orientation θ , and the azimuthal angle ϕ . To arrive at a quantum mechanical solution, we use the TDWP method [73] to solve the time-dependent Schrödinger equation,

$$i \frac{\partial \Psi}{\partial t} = \hat{H} \Psi. \quad (4.10)$$

The 6D Hamiltonian operator including the translational, vibrational, rotational and potential energy terms is given by [11]

$$\hat{H}_{6D} = -\frac{1}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu r^2} + V_{6D}(X, Y, Z, r, \theta, \phi). \quad (4.11)$$

Here, M is the mass of H_2 molecule, and μ is the reduced mass associated with the vibrational motion. V_{6D} is the 6D Grow potential discussed in Section 4.2.2, with the potential energy values extended from the triangle [1/8 of the (2×2) unit cell] into the whole $(\sqrt{2} \times \sqrt{2})$ square unit cell by using appropriate displacements and rotations (according to symmetry).

In this chapter, a pseudo-spectral method is used to propagate the wave packet, in which the Hamiltonian is symmetrically decomposed as a non-commutative form by using the split-operator (SPO) method [74]. The error per time step(Δt) is proportional to Δt^3

in the SPO method and it is unconditionally stable [36], *i.e.*, the maximum time step Δt is not determined by the range of eigenvalues of the Hamiltonian, but by the bandwidth of the initial wave packet [11, 36, 74].

In our implementation [36], the initial wave packet is given by the formula,

$$\Psi(X, Y, Z, r, \theta, \phi) = \Phi_{vj}(r) Y_{jm_j}(\theta, \phi) \frac{1}{\sqrt{A}} e^{i\vec{K}_0 \cdot \vec{R}} \int dk_z b(k_z) \frac{1}{2\pi} e^{ik_z Z}. \quad (4.12)$$

Here, $\Phi_{vj}(r)$ and $Y_{jm_j}(\theta, \phi)$ are the H_2 vibrational and rotational eigenfunction respectively, and v, j and m_j are the corresponding rovibrational quantum numbers. The initial parallel motion of the wave packet along X and Y is described by $(1/\sqrt{A})e^{i\vec{K}_0 \cdot \vec{R}}$, in which A is a normalization factor (the surface area of the surface unit cell), $\vec{K}_0$ is the initial parallel momentum and $\vec{R}$ the position vector (X, Y) . The wave packet describing motion in the Z direction is a function of the initial momentum k_z , and is defined by,

$$b(k_z) = \frac{2\zeta^2}{\pi} e^{-(k_{av}-k_z)^2 \zeta^2 + i(k_{av}-k_z)Z_0}, \quad (4.13)$$

in which ζ is a width parameter, k_{av} is the average momentum in Z , and Z_0 is the center of the initial wave packet in coordinate space.

In this chapter, only normal incidence is considered and thus $\vec{K}_0 = 0$. Two initial wave packets with H_2 in its rovibrational ground state are propagated to obtain results for two kinetic energy ranges, *i.e.*, 50 – 350 meV and 300 – 850 meV. More computational details are listed in Table 4.2, and the method used is described fully in Ref. [36] and Chapter 2.7. The converged grid spacings for Z and r are found to be 0.15 a.u. and 0.085 a.u. in the high energy range, respectively, see Table 4.2.

The discrete potential energy values and the wave packet are defined on the same grid using the DVR-FBR representations [75, 76]. The wave function on X, Y, Z and r is represented by the Fourier representation (DVR), effectively using a plane-wave basis-set. The angular momentum part of the wave function is represented by a finite basis representation (FBR), using orthogonal normalized associated Legendre polynomials as basis functions. Gauss-Legendre and Fourier transformations are used to transform the wave function from the FBR to the DVR [77, 78]. Quadratic form optical potentials [79] are employed with strength parameters such that the reflection from and transmission through the optical potential is minimal.

Finally, the wave packet is asymptotically analyzed by the Balint-Kurti formalism [80–83], in which the scattered wave packet is projected at $Z = Z_\infty$ onto the free particle states. The scattering probability at an incident energy E_{kin} for a transition from the initial state to the final state can be obtained from the S-matrix by,

$$P_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin}) = |S_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin})|^2. \quad (4.14)$$

Table 4.2: Parameters used for 6D quantum dynamics for the low energy interval wave packet (50 – 350 meV) and the high energy interval wave packet (300 – 850 meV) for the initial rovibrational ground state ($v = 0$, $j = 0$, $m_j = 0$). Both distance and time are in atomic unit (a.u.), and energies are in eV, unless indicated otherwise.

Parameters	50 – 350 meV	300 – 850 meV
Initial wave packet		
Center Z_0	9.15	9.15
v	0	0
j	0	0
m_j	0	0
Propagation time step	2.50	1.0
Total propagation time t	115 000	112 000
Scattering grid		
Range of Z Fourier grid	[0, 13.35]	[0, 13.35]
Grid spacing in Z	0.15	0.15
Range of Z optical potential	[7.05, 13.35]	[7.05, 13.35]
Strength of Z optical potential	0.01	0.05
Range of r Fourier grid	[0.41, 7.975]	[0.41, 7.975]
Grid spacing in r	0.085	0.085
Range of r optical potential	[4.15, 7.975]	[4.15, 7.975]
Strength of r optical potential	0.01	0.05
Range of X (Y) Fourier grid	[0, 7.63]	[0, 7.63]
Grid spacing X (Y)	0.186	0.186
Specular grid		
Range of Z Fourier grid	[0, 22.95]	[0, 22.95]
Grid spacing in Z	0.15	0.15
Range of Z optical potential	[12.0, 22.95]	[12.0, 22.95]
Strength of Z optical potential	0.01	0.05
Rotational basis set		
Maximum j in rotational basis	24	28
Maximum m_j in rotational basis	18	18
Analysis		
Z_∞	7.05	7.05

The reaction probability at an incident energy E_{kin} is given by summing up all the scattering probabilities and then subtracting from 1,

$$P_r(E_{kin}) = 1 - \sum_{v'j'm'_jnm} P_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin}). \quad (4.15)$$

4.3 Results and discussion

4.3.1 PES obtained from the “Grow” method

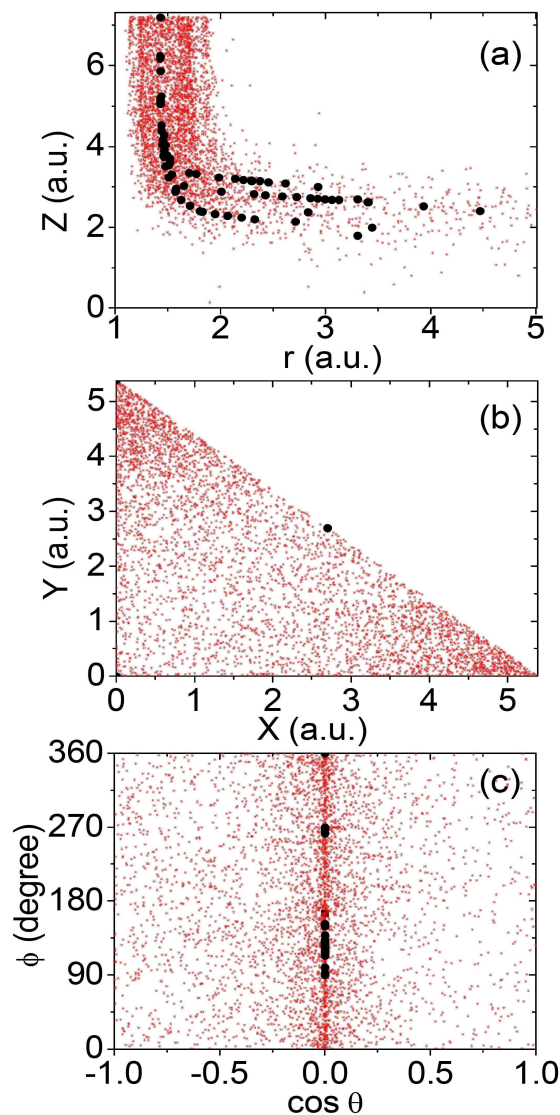


Figure 4.3: Distribution of the data points: (a) projection on (Z, r) ; (b) projection on (X, Y) , where the three corners of the triangle are the same as the three corner atoms in the black triangle of Fig. 4.1(a); and (c) projection on $(\cos \theta, \phi)$. The black filled circles are the initial data points from three reaction paths with H_2 dissociating above top Ti, top Al and hollow sites respectively. The asterisk points are the ones added by the Grow method. The lengths are in atomic units (a.u.).

Analysis of the PES topology is especially useful for the analysis of the reaction mechanism. The distribution of the points in the GROW PES data set is shown in Fig. 4.3. The most frequently visited region by the trajectories is found to be the entrance channel, according to the projection of the points on the (Z, r) coordinates [Fig. 4.3(a)]. Another projection of the data points on (X, Y) [Fig. 4.3(b)], shows that H_2 spends most of its time near the surface Ti atom (Ti top site). The θ anisotropy [the difference between the maximum and minimum value of $V(\theta)$ at fixed values of X, Y, Z, r and ϕ] is 1.40 eV at the molecular adsorption well geometry and 10.80 eV at the minimum barrier geometry. In Fig. 4.3(c), from the $(\cos\theta, \phi)$ projection, most data points are located at the configuration where the θ angle is close to 90° , due to the large anisotropy of the potential with respect to θ (the H_2 molecule prefers to dissociate when the molecule is parallel to the surface). In contrast, the data are almost homogeneously distributed over ϕ which indicates that changing ϕ has little influence on the molecule-surface interaction. The ϕ anisotropy is 0.01 eV at the well geometry, and 0.12 eV at the barrier geometry, in agreement with the distribution of the data in ϕ . With higher density of the data point distribution in these dynamically interesting regions, these regions have higher precision of the potential in the scheme of Bayesian analysis of Eq. 4.6.

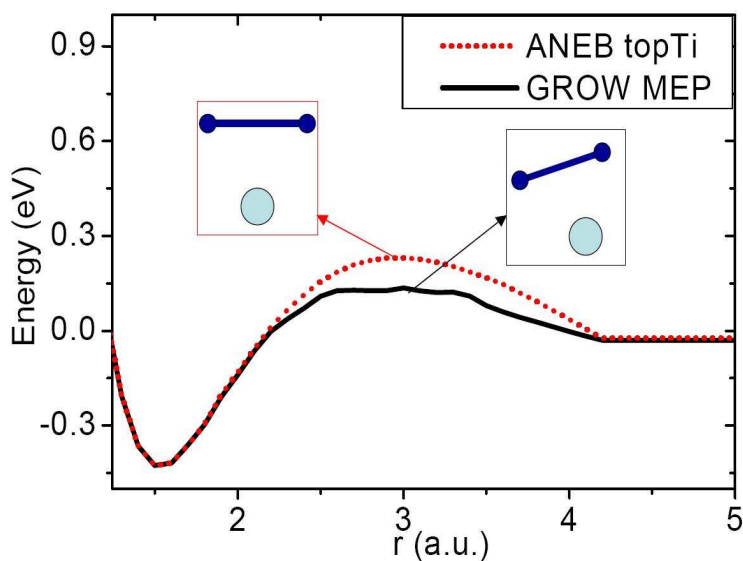


Figure 4.4: *Energies along the MEP as obtained from the Grow potential as shown by the solid line, as well as the reaction path for H_2 dissociating above a top Ti atom. The inset configurations illustrate that the lowest barrier geometry for H_2 dissociating along the MEP is tilted, while in the one dissociating above the Ti atom H_2 always remains parallel to the surface.*

Using the procedure introduced in Section 4.2.2, the 6D PES was obtained by MS interpolation. The one-dimensional potential along the MEP obtained from Grow

is shown in Fig. 4.4. The reaction path from the gas phase to the molecular adsorption well is identical to the one obtained with the adaptive nudged elastic band (ANEb) [84] method. However, the barrier height obtained from the Grow method is only 0.13 eV, and the barrier configuration has an angle of 15° with the surface plane, with the H_2 center of mass (COM) moving away from the Ti top site by 0.55 a.u. along the Ti–Al neighboring line (or X direction). This barrier is 0.10 eV lower than the one we found in the previous Chapter 3 using ANEB calculations (see also Fig. 4.4). In this ANEB barrier search, the COM of H_2 was fixed above the top Ti site and kept parallel to the surface during dissociation. However, for the lower barrier from the Grow potential, H_2 is allowed to relax freely in six DOFs, resulting in the lower barrier position: $X = 0.55$ a.u., $Y = 5.39$ a.u., $Z = 2.41$ a.u., $r = 2.92$ a.u., $\theta = 75^\circ$, and $\phi = 0^\circ$. This lower energy reaction path was first found by Valdes *et al.* [85] using the climbing images nudged elastic band (CINEB) method [86] calculations. When the COM of H_2 is restricted to be above the top Ti site [2], the barrier geometry is $X = 0$ a.u., $Y = 5.39$ a.u., $Z = 2.57$ a.u., $r = 2.99$ a.u., $\theta = 90^\circ$, and $\phi = 0^\circ$, and has a barrier of 0.23 eV.

The two-dimensional (2D) cuts through the PES are shown in Fig. 4.5. 2D elbow plots for H_2 dissociating along the MEP and the top Ti site are shown in Fig. 4.5(a) Fig. 4.5(b) respectively. The 2D cut along the MEP corresponds to the one-dimensional plot in Fig. 4.4 with a well depth of 0.43 eV and a barrier height 0.13 eV. Fig. 4.5(c) and Fig. 4.5(d), show that the barrier for H_2 dissociation is much higher above the Al top site and the hollow site, respectively. In figure Fig. 4.5(e) and Fig. 4.5(f) 2D cuts along (X , Y) are shown, fixing r at the bond length of molecular adsorption well value and barrier position value while relaxing θ and ϕ , respectively. In Fig. 4.5(f), four potential wells (at 0.55 a.u. away from the middle of the unit cell) can be found around the Ti atom (in the middle of the unit cell), corresponding to the barrier positions of H_2 dissociation.

4.3.2 Quasi-classical H_2 dissociation probabilities

On the PES constructed from the MS interpolation method, 6D quasi-classical dynamical trajectory calculations are performed, in which the ZPE of the H_2 molecule is considered. Reaction probabilities are obtained for the following initial H_2 states (see Fig. 4.6): the rovibrational ground state ($v = 0$, $j = 0$), the cartwheel rotationally excited state ($v = 0$, $j = 4$, $m_j = 0$), the helicopter rotationally excited state ($v = 0$, $j = 4$, $m_j = 4$), and the first vibrationally excited state ($v = 1$, $j = 0$). For each H_2 initial state, calculations are carried out for 100 incident energies, with equal spacing in the range from 0.03 to 1.50 eV, and for each incident energy point 5000 trajectories are run.

The QCT results in Fig. 4.6 show that the reaction probability increases with the incident energy except for minor fluctuations due to statistical errors. The helicopter rotationally excited state ($j = 4$, $m_j = 4$) has slightly higher reaction probabilities than

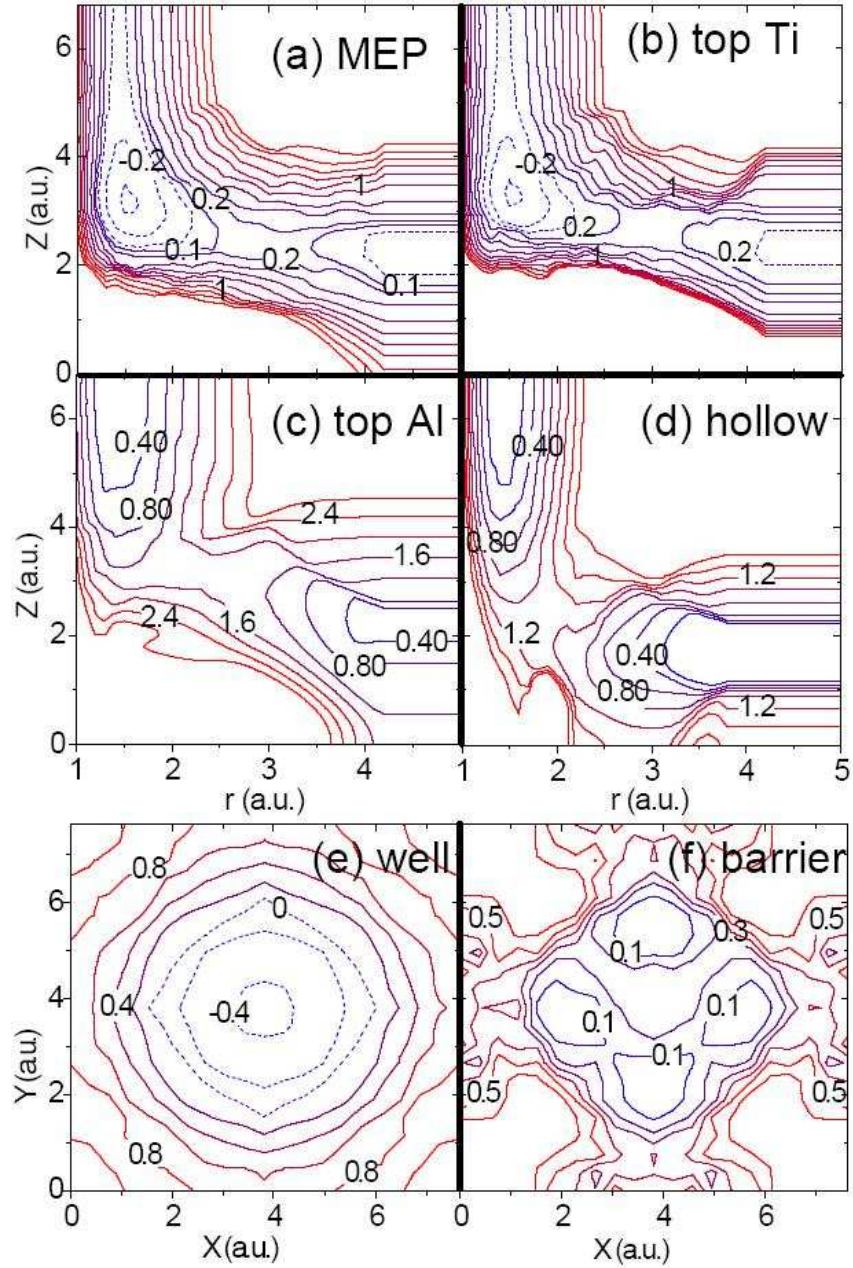


Figure 4.5: (a) PES 2D cut at (Z, r) along the MEP (X, Y, θ and ϕ are fully relaxed); (b) 2D cut at (Z, r) with COM fixed above the top Ti, $\theta = 90^\circ$ and $\phi = 0.0^\circ$; (c) same as (b) fixed at top Al; (d) same as (b) fixed at hollow site. Figure (e) and (f), the 2D cuts along (X, Y) when r is fixed at the well and barrier $H-H$ distance, respectively with relaxation of θ and ϕ .

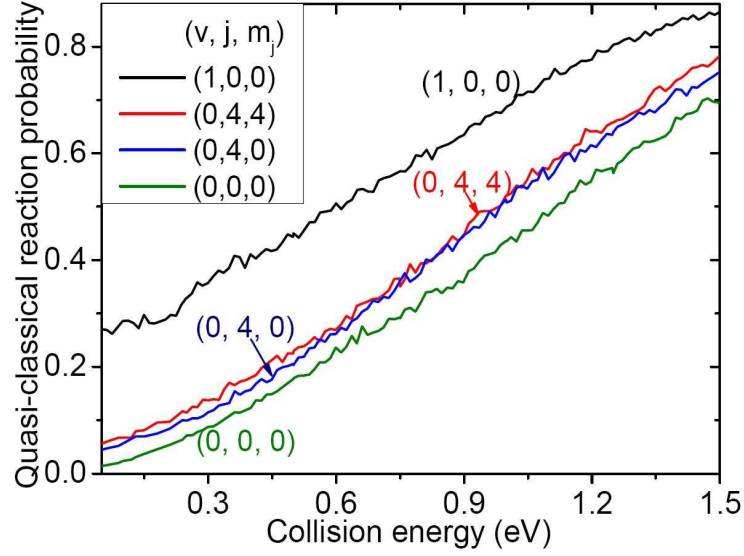


Figure 4.6: Quasi-classical reaction probability for the para- H_2 rovibrational ground state ($v = 0, j = 0, m_j = 0$) (black solid line), the cartwheel rotationally excited state ($v = 0, j = 4, m_j = 0$) (dotted line), the helicopter rotationally excited state ($v = 0, j = 4, m_j = 4$) (dashed line) and the first vibrationally excited state ($v = 1, j = 0, m_j = 0$) (bold line). The collision energies are sampled from 0.03 – 1.50 eV. The error bars plotted represent one sigma interval (binomial standard deviation).

the cartwheel rotationally excited state ($j = 4, m_j = 0$), but the differences are small *i.e.*, within 3.0 %. Vibrational excitation has a large efficacy for promoting reaction over the entire range of incident energies.

The distribution of mean number of rebounds (N_{reb}) counted from each QCT as a function of the collision energy, for the four different initial states, is shown in Fig. 4.7. A rebound occurs if the velocity of H_2 in the Z -direction changes from negative to positive, thus $N_{reb} > 1$ is an indication of trapping. In Fig. 4.7(a), a general trend observed is that N_{reb} decreases with increasing collision energy. N_{reb} assumes the largest values for the ($v = 0, j = 0$) state. At low collision energy ($E_{kin} = 0.10$ eV), N_{reb} is 4.66 for dissociating ($v = 0, j = 0$) H_2 , the value decreasing to 1.37 at $E_{kin} = 0.90$ eV. This finding indicates that in the low energy trajectories dissociation is promoted by trapping. During this trapping, configuration of the H_2 molecule can be adjusted to a proper orientation to pass the barrier. However, for large incident energy (*i.e.*, $E_{kin} = 0.90$ eV), the majority of the trajectories have $N_{reb} = 1$. In general, the higher energy trajectories can pass the barrier with less rebounds, especially for the vibrationally excited state ($v = 1, j = 0$), see Fig. 4.7(a). The number of rebounds of the vibrationally excited state is relatively less sensitive to the collision energy. For this state, N_{reb} decreases from 1.85 to 0.95, for $E_{kin} = 0.10$ eV and $E_{kin} = 0.90$ eV respectively. From the comparison of the N_{reb} values of $v = 0$ and $v = 1$,

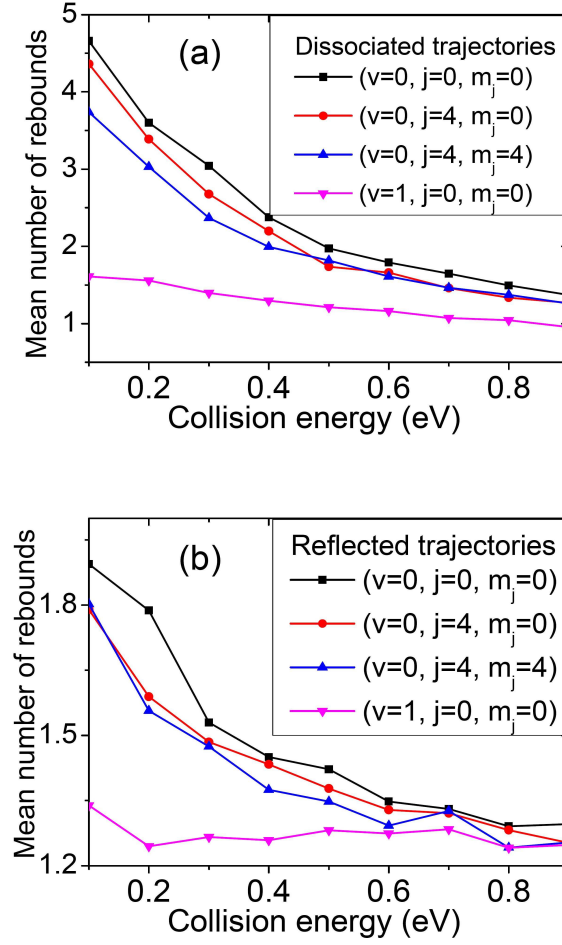


Figure 4.7: Mean number of rebounds occurring in the QCTs for the reacted trajectories (a) and the reflected trajectories (b), for four initial states. A rebound occurs if the velocity in the Z direction changes from negative to positive.

we see that $v = 1$ H_2 is more likely to dissociate with less rebounds due to its larger initial vibrational energy, *i.e.*, it is more unlikely to be trapped in the molecular adsorption well before dissociation occurs.

The trajectories of reacting H_2 in the rotationally excited states ($j = 4, m_j = 0$) and ($j = 4, m_j = 4$) have slightly lower N_{reb} values than the ($v = 0, j = 0$) state, by about 0.30 and 0.60, respectively, when the collision energy is below 0.40 eV, [see Fig. 4.7(a)].

For the reflected trajectories in Fig. 4.7(b), N_{reb} has much smaller values at low collision energy for the ($v = 0, j = 0$) rovibrational ground state, cartwheel and helicopter rotationally excited states. At $E_{kin} = 0.10$ eV, N_{reb} of the reflected trajectories is only 1.89 for the ($v = 0, j = 0$) state [$N_{reb} = 4.66$ for dissociating ($v = 0, j = 0$) H_2]. The comparison

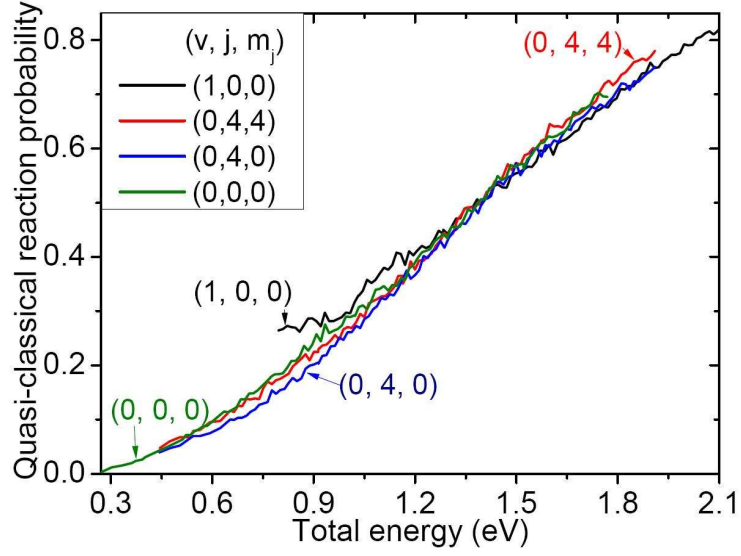


Figure 4.8: Reaction probability computed with quasi-classical dynamics but plotted as a function of the total (internal and translational) energy.

of the two panels in Fig. 4.7 is consistent with the conclusion that in the less trapped trajectories H_2 is more likely to be reflected to the gas phase at low incident energies for these three states. Increasing the collisional, vibrational and rotational energies all increase the chance of direct dissociation.

At low incident energy, trapping of the H_2 molecule is the main mechanism leading to dissociation for the rovibrational ground state ($v = 0$, $j = 0$). Similar results were previously obtained for the $H_2 + \text{Pt}(211)$ [37, 87], $H_2 + \text{Pd}(111)$ [88] and $H_2 + \text{Pd}(110)$ [89] systems, in which trapping promotes reaction by providing the system with a longer time to reach an optimal configuration to overcome the barrier.

The rotational efficacy $\Theta_r(P_r)$ and the vibrational efficacy $\Theta_v(P_r)$ [90, 91], may be calculated from

$$\begin{aligned}\Theta_r(P_r) &= \frac{E_{kin}^{j=0}(P_r) - E_{kin}^{j=4}(P_r)}{E_{rot}(j=4) - E_{rot}(j=0)}, \\ \Theta_v(P_r) &= \frac{E_{kin}^{v=0}(P_r) - E_{kin}^{v=1}(P_r)}{E_{vib}(v=1) - E_{vib}(v=0)}.\end{aligned}\quad (4.16)$$

Here, E_{kin}^j (E_{kin}^v) is the translational energy required to obtain a reaction probability P_r when the H_2 molecule is initially in the rotational (vibrational) state j (v), and E_{rot} (E_{vib}) is the rotational (vibrational) energy of the H_2 molecule in the gas phase. An efficacy value of $\Theta_r(P_r)$ [$\Theta_v(P_r)$] larger than 1.0 means that putting energy into rotation (vibration) is more efficient at promoting reaction than putting energy into translation. The opposite is

true for a values less than 1.0.

Using these two formulae, both the rotational and vibrational efficacy can be obtained from the reaction probability curves in Fig. 4.6. In the entire energy reaction range considered, the rotational efficacy $\Theta_r(P_r)$ is close to 1.0, for both the cartwheel and the helicopter rotationally excited states. This means that rotational energy is as effective at promoting the dissociation as translational energy. The vibrational efficacy is also close to 1.0 in the entire energy reaction range. However, $\Theta_v(P_r) = 1.20$ when the dissociation probability is below 30.0 %, which indicates that putting energy into vibration could make the H_2 molecule circumvent the barrier in a more efficient way than possible by putting energy into translation. The vibrational efficacy decreases with increasing dissociation probability. At a dissociation probability of 50.0 %, the $\Theta_v(P_r)$ is around 1.0.

The reaction probability curves are re-plotted in Fig. 4.8 as a function of the total (internal and translational) energy. From this figure, it is seen that the H_2 dissociation probably mainly depends on the total energy and less on how the energy is divided between translation, rotation and vibration.

The fact that the $H_2 + \text{Ti/Al(100)}$ system, which has a deep well in front of the barrier, has a rotational and vibrational efficacy close to 1.0 suggests that the total (internal and translational) energy undergoes complete randomization in the initial conditions (translational, rotational and vibrational energy), making the reaction rate solely depend on the energy. This agrees with the micro-canonical unimolecular rate theory of dissociative chemisorption for CH_4 on Ni(100) developed by Harrison and coworkers [22], suggesting that it should be possible to compute accurate reaction rates with this theory.

4.3.3 Quantum dynamics of H_2 dissociation probability

Quantum dynamical calculations on the $H_2 + \text{Ti/Al(100)}$ reaction have been carried out for normal incidence of H_2 in its ($v = 0$, $j = 0$, $m_j = 0$) state.

The converged quantum reaction probability for H_2 dissociation is plotted in Fig. 4.9. Corresponding quasi-classical and pure classical reaction probabilities (the latter one with $E_{vib} = 0$ eV) are also shown in this figure. The quantum reaction probability shows fluctuations in the low energy range, which may be explained by resonances (the molecule has extra time to tunnel through the barrier when trapped in a metastable state leading to dissociation at the corresponding energies). The results of the quantum dynamics calculation agree well with the quasi-classical ones in the low energy interval 50 – 200 meV, but the quantum dissociation probabilities are higher than the quasi-classical results by up to 0.06 (corresponding to a relative difference of 30.0 %) for incident energies larger than 200 meV. The difference between quasi-classical and quantum reaction probabilities presumably tells us that the randomization of the energy in a quasi-classical trajectory may hinder the H_2 dissociation, especially at high incident energies. Classical dynamics

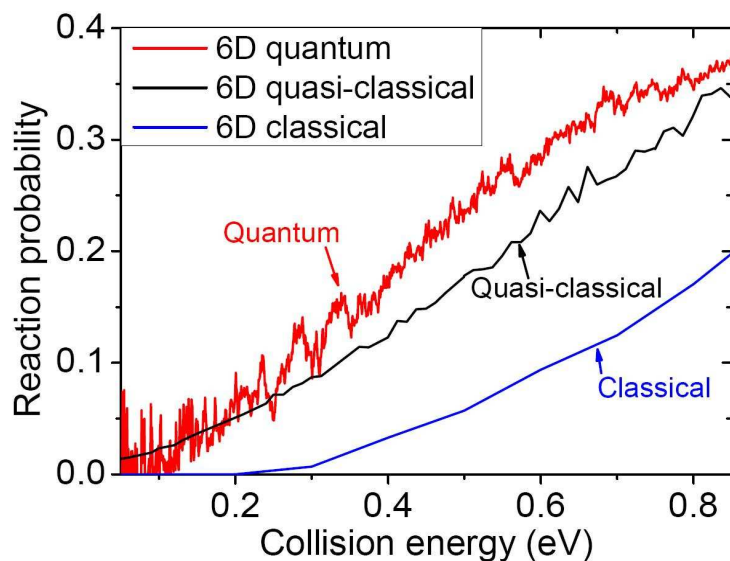


Figure 4.9: Quantum reaction probability for H_2 initially in its ground rovibrational state ($v = 0$, $j = 0$, $m_j = 0$). The quasi-classical and the classical results are also plotted.

results (see Fig. 4.9) show a reaction probability that is zero when E_{kin} is below 0.20 eV.

To illustrate the development of the wave function in time, the projected probability density on the 2D (Z , r) grid is shown in Fig. 4.10 and Fig. 4.11. In Fig. 4.10(a–f) of the low incident energy (50 – 350 meV) wave packet, two nodes start to appear in the Z direction after the wave packet makes contact with the surface at $t = 2500$ a.u. [see Fig. 4.10(b)]. At $t = 5000$ a.u. [see Fig. 4.10(c)], the majority of the wave packet has hit the surface and is escaping from the surface to the gas phase, which contains a norm of 98.9 % at this snapshot and more blobs in Z coordinates are clearly visible. Each blob has different kinetic energy to escape from the surface and the gaps between the blobs correspond to rotational excitation and trapping (which are not visible by eye in the plots at the earlier stage of propagation due to the small quantity). The dynamic process at the low incident energy is dominated by reflection in which the rotational (de-) excitation plays an important role.

In the wave packet dissociated by the high energy range [300 – 850 meV, see Fig. 4.11(a–f)], the most interesting phenomenon found from the propagation of the wave packet is that a node clearly appears in r when the propagation time $t = 4000$ a.u. [Fig. 4.11(d)] and this node remains during the process of propagation. At $t = 6000$ a.u., only the $v' = 1$ state can be observed in the entrance channel, and at this time 61.4 % of the norm of the wave packet is still present in the strong interaction region (entrance channel and the molecular adsorption well) of the scattering grid. Although, $P(v = 0, j = 0 \rightarrow v' = 1)$ is only 6.0 %, the results suggest that trapping in the molecular adsorption well can

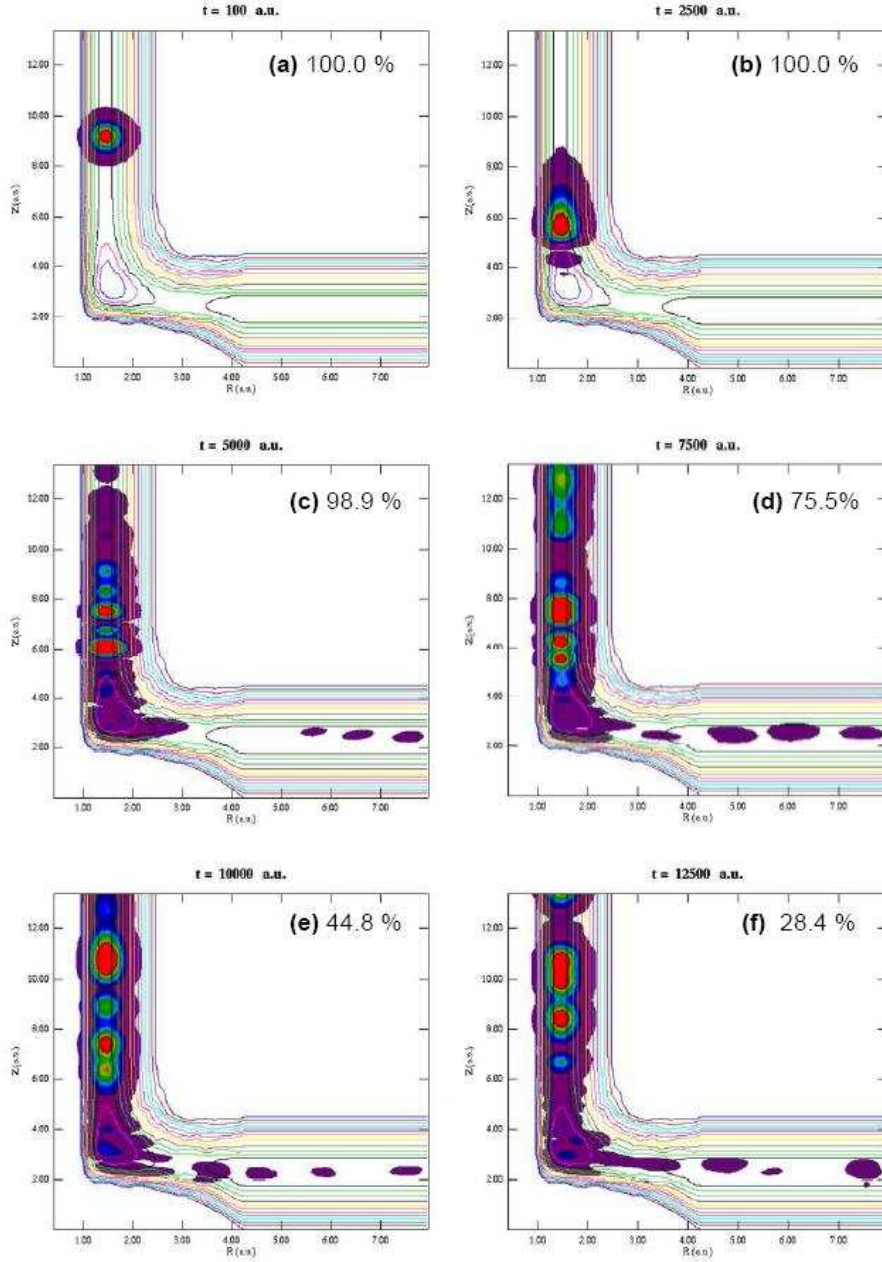


Figure 4.10: Snapshots of the probability density with respect to the propagate time from $t = 100$ a.u. to $t = 12500$ a.u. for low collision energy range 50 – 350 meV. The probability density is given by $\Psi(Z, r)\Psi(Z, r)^*$, in which the $\Psi(Z, r)$ is the projection of the 6D wave packet on 2D (Z, r) grid with respect to $(j' = 0, m'_j = 0, n' = 0, m' = 0)$. The background of the plot is the 2D PES along the MEP, shown in Fig. 4.5(a).

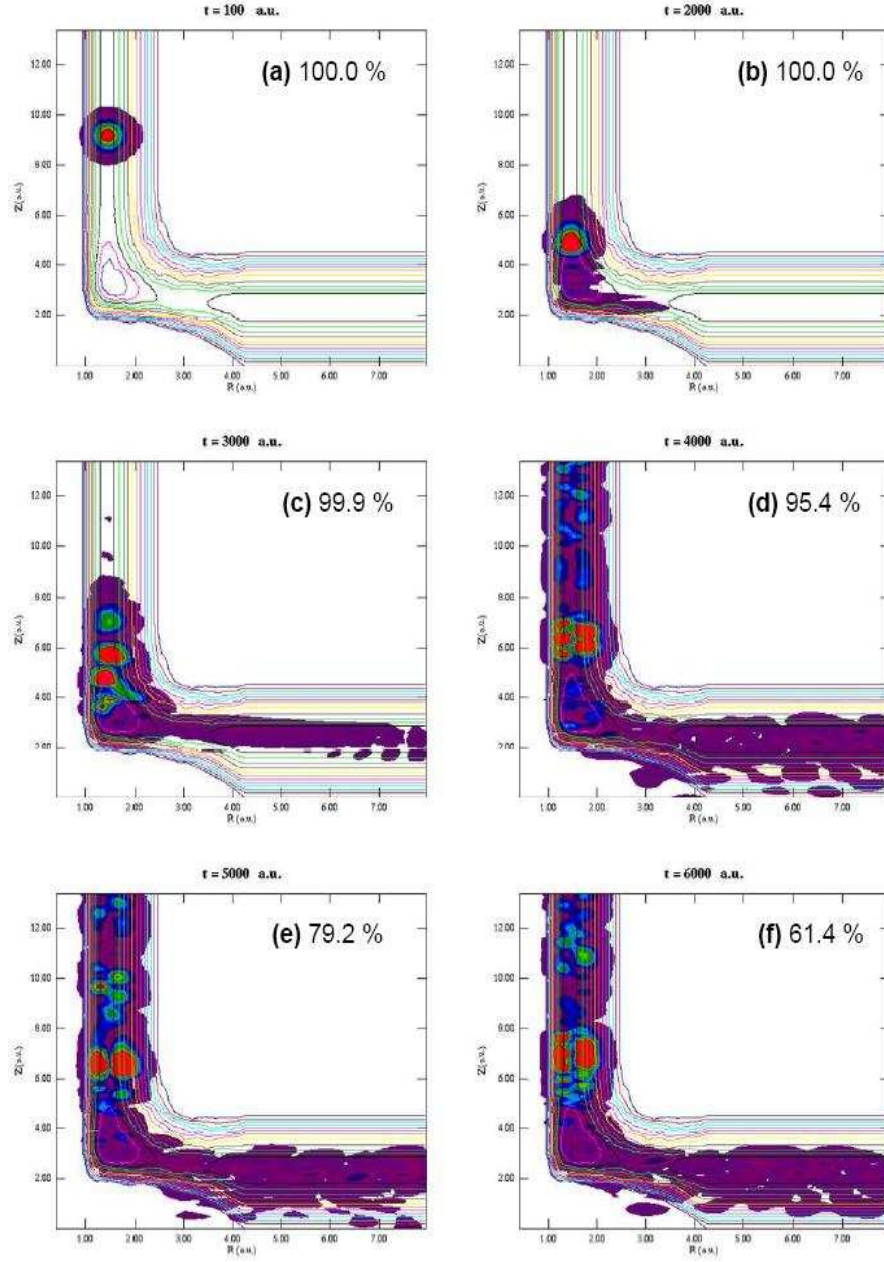


Figure 4.11: Snapshots of the TDWP probability density as a function of Z and r for different propagation times in the range 100 – 6000 a.u., for the high collision energy range 300 – 850 meV. The probability density is given by $\Psi(Z, r)\Psi(Z, r)^*$, in which the $\Psi(Z, r)$ is the projection of the 6D wave packet on 2D (Z, r) grid for $(j' = 0, m'_j = 0, n' = 0, m' = 0)$.

arise from the vibrational excitation of H_2 .

4.4 Conclusions

In this chapter, based on the density functional theory, we studied the elementary reaction of H_2 dissociation on a 1 ML Ti covered Al(100) surface. Firstly, the Grow method is applied to build a 6D electronic ground state PES using the BO and static surface approximations. H_2 dissociation probabilities are calculated through both the CT and QCT methods and the TDWP method. The dynamically interesting region is found to be at the Ti site of the surface where the molecular adsorption well in the MEP is located, leading to a high density of data points in this region with the Grow method. The MEP has been improved in the Grow PES. The new H_2 dissociation barrier is found to be 0.13 eV, which is 0.10 eV lower than the one reported in previous Chapter 3.

In the quasi-classical dynamics, we have calculated the dissociation probabilities for four initial quantum states of H_2 , *i.e.*: $(v = 0, j = 0)$, $(v = 0, j = 4, m_j = 0)$, $(v = 0, j = 4, m_j = 4)$, and the vibrationally excited state $(v = 1, j = 0)$. The dissociated trajectories for low incident energies (*i.e.*, below 0.20 eV) of the rovibrational ground state and the rotationally excited states have relatively large N_{reb} values (between 3 – 5), which indicates that these trajectories are trapped before dissociation. In contrast, the molecule in its vibrationally excited state dissociates more directly. Both rotational and vibrational excitation promote direct H_2 dissociation efficiently, with an efficacy of approximately 1.

The presence of the deep adsorption well in front of the barrier leads to statistical behavior: the H_2 dissociation probability depends only on the total (internal and translational) energy, except that the vibrational efficacy is somewhat larger than 1.0 in the low reaction probability region.

The reaction of H_2 in its rovibrational ground state $(v = 0, j = 0)$ is also considered using quantum dynamics. The calculations show that the QCT method describes the reaction more accurately than the CT method, as found earlier for most H_2 + metal surface systems studied.

In summary, based on the evidence that Ti plays a role in the process of hydrogen storage in $NaAlH_4$, we theoretically calculated the H_2 dissociation probability on a 1 ML Ti covered Ti/Al(100) surface. We hope that our predictions of the reaction probability curves can be confirmed by molecular beam experiments.

4.5 References

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Chapter 5

Dynamics of H₂ dissociation on the 1/2 ML Ti-covered c(2 × 2)-Ti/Al(100) surface

This chapter is based on:

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Abstract

The dissociation of H₂ on Ti-covered Al surfaces is relevant to the rehydrogenation and dehydrogenation of the NaAlH₄ hydrogen storage material. The energetically most stable structure for a 1/2 monolayer of Ti deposited on the Al(100) surface has the Ti atoms in the second layer with a c(2 × 2) structure, as has been confirmed by both low-energy electron diffraction and low-energy ion scattering experiments and density functional theory studies. In this work, we investigate the dynamics of H₂ dissociation on a slab model of this Ti/Al(100) surface. Two six-dimensional potential energy surfaces (PESs) have been built for this H₂ + Ti/Al(100) system, based on the density functional theory PW91 and RPBE exchange-correlation functionals. In the PW91 (RPBE) PES, the lowest H₂ dissociation barrier is found to be 0.65 (0.84) eV, with the minimum energy path occurring for H₂ dissociating above the bridge to top sites. Using both PESs, H₂ dissociation probabilities are calculated using the classical trajectory, the quasi-classical trajectory (QCT), and the time-dependent wave-packet methods. We find that the QCT H₂ dissociation probabilities are in good agreement with the quantum dynamics results in the collision energy range studied, up to 1.0 eV. We have also performed molecular beam simulations and present predictions for molecular beam experiments. Our molecular beam simulations show that H₂ dissociation on the 1/2 ML Ti/Al(100) surface is an activated process, and the reaction probability is found to be 6.9 % for the PW91 functional and 1.8 % for the

RPBE at a nozzle temperature of 1700 K. Finally, we have also calculated H_2 dissociation rate constants using transition state theory and the QCT method, which could be relevant to modeling Ti-catalyzed rehydrogenation and dehydrogenation of the $NaAlH_4$.

5.1 Introduction

One of the fundamental questions in the hydrogen storage material sodium alanate ($NaAlH_4$) [1] is what the catalytic role of titanium is. Isotope exchange and scrambling experiments [2, 3] on both absorption and desorption of H_2 in Ti-doped $NaAlH_4$ suggest that Ti promoted diffusion of heavier hydrogen-containing species, such as AlH_x or NaH , represents the rate limiting step in H_2 release and uptake. However, it seems likely that Ti should also catalyze H_2 dissociative adsorption (and the reverse process, associative desorption), even though this is not the most important aspect of its catalytic activity. Several experimental studies have found Ti to be present in Al as a Ti-Al alloy of varying compositions [4–10], and it is now clear that most of the Ti present should be in this form during cycling [11]. A detailed summary of the different possible roles played by Ti and where it is thought to reside in the material is given in Refs. [12–16]. In the present contribution our focus is on the dissociation dynamics of molecular hydrogen on the energetically most stable structure for one half monolayer (ML) of Ti deposited on an Al(100) surface, a relevant model system for studying the dehydrogenation and rehydrogenation dynamics of Ti-doped $NaAlH_4$.

Growth of an fcc Ti phase on Al(100) surface is favorable at low Ti coverage [17, 18]. Low-energy electron diffraction experiments by Kim *et al.* [17] show that Ti atom deposition on a clean Al(100) surface results in a $c(2 \times 2)$ pattern, with the Ti atoms probably residing in the second layer of the substrate. Saleh *et al.* [18] has confirmed that up to 1/2 ML Ti coverage the surface Al atoms float on top of the Ti film, by low-energy ion scattering measurements.

Theoretically, molecular hydrogen dissociation on pure Al surfaces is found to be kinetically unfavorable. The lowest energy barriers for H_2 dissociation on pure Al surfaces obtained with density functional theory (DFT) at the generalized gradient approximation level are 1.28 eV on Al(111) [19], 1.0 eV on Al(100) [20, 21], and 0.70 eV on Al(110) [22]. As Ti/Al(100) surfaces represent a sensible choice for modeling (a part of) the dehydrogenation and rehydrogenation dynamics of Ti-doped $NaAlH_4$, several Ti/Al(100) surfaces have been studied theoretically [20, 21, 23–25], with Ti coverages varying from 1/18 to 1 ML. The most stable Ti/Al(100) surface was found when 1/2 ML of Ti is placed in the second layer of the Al(100) surface, which has a H_2 dissociation barrier of 0.63 eV [21, 26]. The second most stable Ti/Al(100) surface is found to be when 1 ML of Ti is placed in the first and third layers of Al(100). This structure has a lower H_2 dissociation barrier of 0.13 eV [21, 26], and a deep molecular adsorption well

with a depth of 0.45 eV in front of the barrier.

In describing the hydrogen dissociation dynamics on Ti/Al(100) surface, the Born-Oppenheimer (BO) approximation has been applied. This approximation has been found to accurately describe the dissociation of H_2 on metal surfaces [27], because H_2 has a low electron affinity and the net charge transfer is almost zero during the process of dissociation [27, 28]. Thus, we neglect electron-hole pair excitations. Due to the mismatch between the mass of H_2 and surface Ti and Al atoms, the energy transfer from the molecule to the metal surface should be small and unlikely to influence the scattering results. Therefore, the Ti/Al(100) slab can be fixed during the process of H_2 dissociation, and we only consider the motion in the six hydrogen degrees of freedom on the electronic ground state potential energy surface (PES).

Six-dimensional (6D) quantum dynamics (QD) of gas-surface reactions has a history of more than fifteen years [29–36], and it has been successfully implemented to address the dissociative chemisorption of H_2 on metal surfaces, *i.e.*, H_2 on Pd(100) [29, 37], Pd(110) [38], Rh(100) [37], Cu(100) [34], Cu(111) [30, 32, 39–41], Pt(111) [27, 42], Pt(211) [43], Pd(111) [44], Ru(0001) [45], NiAl(110) [46], and on sulfur-precovered Pd(100) [47] and CO-precovered Ru(0001) [48].

Reactions proceeding over deep potential energy wells can be treated statistically, if the intermediates are sufficiently long lived [49, 50]. A treatment of the formation and decay of the intermediates into reactant and product channels may be enough to give satisfactory results [51, 52]. A quasi-classical trajectory (QCT) study [26] showed that H_2 dissociation on the 1 ML (2×2)-Ti/Al(100) surface, which is affected by a deep well (with depth of 0.45 eV) in front of the barrier, has a rotational and vibrational efficacy close to 1.0. This suggests that the total (internal and translational) energy undergoes complete randomization with respect to the initial conditions (translational, rotational and vibrational energy), making the reaction rate solely depend on the total energy [21, 26]. Such a system can therefore be described with the micro-canonical unimolecular rate theory of dissociative chemisorption developed by Harrison and coworkers [53].

However, the 1 ML (2×2)-Ti/Al(100) surface has a slightly higher (less stable) Ti binding energy than the 1/2 ML Ti-covered (with Ti in the second layer of the slab) Al(100) surface [21]. Due to the higher stability of the 1/2 ML coverage system, it might be a more appropriate model system for the dehydrogenation and rehydrogenation dynamics of Ti-doped $NaAlH_4$ and also easier to study in molecular beam experiments. The aim of the present work is therefore to investigate the dynamics of this 1/2 ML H_2 + Ti/Al(100) system, and to make predictions for such experiments.

Based on a slab model of 1/2 ML Ti/Al(100) surface [21], two 6D PESs have been built by DFT [54, 55]. Classical trajectory (CT), QCT and time-dependent wave-packet (TDWP) calculations are performed on the two PESs. Our results show that the H_2 dissociation probabilities obtained from the QCT and the QD agree well with each other in the

whole collision energy range studied, up to 1.0 eV. Molecular beam simulations [39, 48] illustrate that H_2 dissociation on 1/2 ML Ti/Al(100) surface is activated, and with the beam parameters used the reaction probability for PW91 (RPBE) functional is only 6.9 % (1.8 %) at a high nozzle temperature of 1700 K. The H_2 dissociation rate constants are also calculated from transition state theory (TST) [56, 57] and QCT reaction probabilities.

The layout of the paper is as follows: The methodology and numerical details are presented in Section 5.2. Results are presented and discussed in Section 5.3. Finally, conclusions and an outlook are given in Section 5.4.

5.2 Methodology and numerical details

5.2.1 Electronic structure calculations and slab model

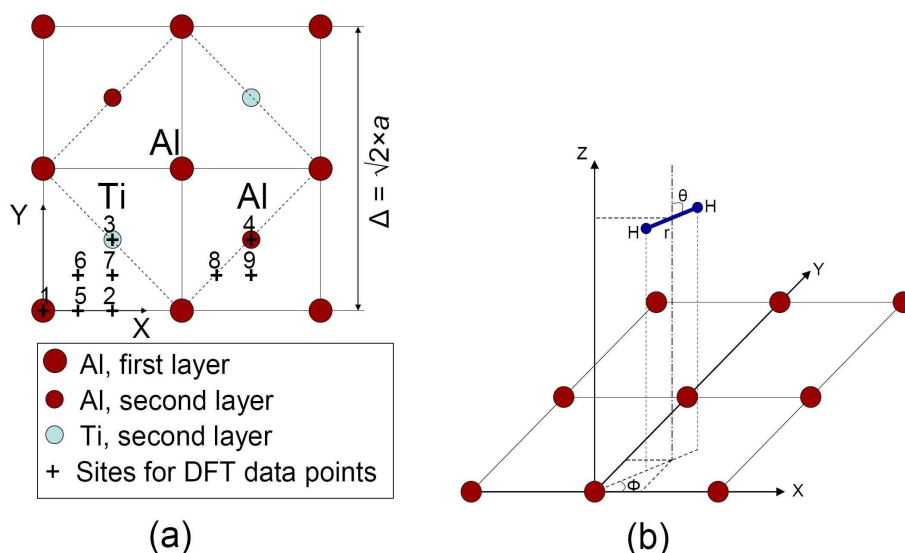


Figure 5.1: (a) (2×2) surface unit cell of Ti/Al(100) with lattice constant $a = 4.04$ Å, $\Delta = \sqrt{2} \times a$. The brown and blue spheres represent Al and Ti atoms, respectively. The nine sites marked by “+” symbols are the positions for which DFT calculations were performed. The $(\sqrt{2} \times \sqrt{2})R45^\circ$ unit cell is shown by the dotted lines. (b) The coordinates used for $H_2 + \text{Ti/Al(100)}$: the H–H distance r , the position of the H_2 COM over the alloy surface (X, Y, Z) , the polar angle θ , and the azimuthal angle ϕ .

The DFT code Vienna *ab-initio* simulation package (VASP) [58–60] is used to study H_2 dissociation on the 1/2 ML $c(2 \times 2)$ - Ti/Al(100) slab model with Ti atoms in the second layer. Both the PW91 functional [61] and the RPBE functional [62] are employed

to describe the exchange-correlation energies. The interaction between ions and electrons is described by the projector-augmented wave (PAW) method [63]. A plane wave basis set is used for the electronic orbitals, with a cutoff energy of 350 eV. Fermi-Dirac smearing [64] is applied with an electronic temperature T of $k_B T = 0.10$ eV (k_B is the Boltzmann constant). The Brillouin zone is sampled by the Monkhorst-Pack [65] method, using a set of $8 \times 8 \times 1$ k -points. The convergence tests of the plane wave cutoff energy and number of k -points are shown in Table 5.1. In the Z direction (perpendicular to the surface, see Fig. 5.1), a vacuum layer of 15.0 Å was placed between the slabs to avoid artificial interactions caused by the periodic boundary conditions. The lattice constant of the surface unit cell is $a = 4.04$ Å. More details of the slab structure can be found in Ref. [21]. A four-layer Ti/Al(100) slab model is employed in this work to study the H_2 dissociation dynamics (see Fig. 5.1), using a (2×2) unit cell. The overall convergence of the molecule-surface interaction energy with respect to all these computational parameters is about 0.1 eV.

Table 5.1: Convergence tests for the plane wave cutoff energy E_{cut} and number of k -points for the momentum in the directions of X , Y and Z , and their influence on the value of H_2 dissociation CINEB barrier heights for PW91 (E_b^{PW91}) and RPBE (E_b^{RPBE}) functionals.

k -points	E_{cut} (eV)	E_b^{PW91} (eV)	E_b^{RPBE} (eV)
$5 \times 5 \times 1$	350	0.70	0.89
$6 \times 6 \times 1$	350	0.65	0.84
$7 \times 7 \times 1$	350	0.67	0.86
$8 \times 8 \times 1$	350	0.65	0.84
$7 \times 7 \times 1$	450	0.69	0.88
$8 \times 8 \times 1$	450	0.67	0.86

The H_2 dissociation barrier heights presented in Table 5.1 are obtained using the climbing image nudged elastic band (CINEB) [66] method.

According to recent theoretical [45, 67] and experimental [67, 68] work on $H_2 + Ru(0001)$, $H_2 + Cu(111)$ [39], and N_2 on W(100) and W(110) surfaces [69], the RPBE functional [62] typically gives higher dissociation barriers than the PW91 functional [61]. Realistic barrier heights probably fall in between the PW91 and RPBE values [39, 68]. In this paper both PW91 and RPBE functionals are employed to obtain two 6D PESs for the CT, QCT and TDWP calculations.

5.2.2 The interpolation of the 6D PESs

The corrugation reducing procedure (CRP) developed by Busnengo and coworkers [70, 71], has been used to obtain a global PES for the 1/2 ML $H_2 + Ti/Al(100)$ system. The

CRP has been successfully employed for numerous H_2 + surface systems, *e.g.*, H_2 dissociation on Pd(111) [44, 70, 72], Pt(111) [42, 71], Pt(211) [43, 73], Cu(111) [39, 71], Ni(100), Ni(110), Ni(111) [74], NiAl(110) [75], and $c(2 \times 2)$ -Cu/W(100) [76].

Within the CRP, the full 6D molecule-surface interaction potential V_{int}^{6D} is written as the sum of two 3D hydrogen atom-surface potentials R_A^{3D} and R_B^{3D} and the 6D interpolation function I^{6D} [70],

$$V_{int}^{6D}(X, Y, Z, r, \theta, \phi) = I^{6D}(X, Y, Z, r, \theta, \phi) + R_A^{3D}(X_A, Y_A, Z_A) + R_B^{3D}(X_B, Y_B, Z_B). \quad (5.1)$$

Here, the six H_2 coordinates used are the hydrogen intra-molecular distance r , its center of mass coordinates (X, Y, Z) , where Z represents the distance to the surface, the polar angle of orientation θ , and the azimuthal angle ϕ . The coordinates (X_A, Y_A, Z_A) and (X_B, Y_B, Z_B) denote the positions of the two hydrogen atoms, respectively. In the CRP method, to reduce the corrugation of the PES due to the strong repulsion experienced by the H atoms in the H_2 molecule when they are close to the metal surface atoms, one subtracts the two 3D atomic contributions of the atom-surface potentials from V_{int}^{6D} . In this way a smooth 6D interpolation function I^{6D} with low corrugation can be obtained, and this can then be more accurately interpolated.

The 3D atomic H-surface potential R_A^{3D} (R_B^{3D}) is given by [70],

$$R_A^{3D}(X_A, Y_A, Z_A) = I^{3D}(X_A, Y_A, Z_A) + \sum_{i=0}^n Q^{1D}(R_i), \quad (5.2)$$

where R_i is the distance from the H-atom to a metal surface atom labeled by i , and the sum is taken over the n nearest neighbors (9 sites for n are used in this paper). I^{3D} is the 3D interpolation function and Q^{1D} is a 1D reference potential.

To construct the PES, we have computed DFT data points which have been used either as input for the interpolation or for test purposes following the same procedure as that used for the H_2 + NiAl(110) [75] and H_2 + Pd(111) [72] systems.

A. H + Ti/Al(100) 3D PES

According to the $c(2 \times 2)$ symmetry of the 1/2 ML Ti/Al(100) surface, nine different sites in the unit cell are used to interpolate R_B^{3D} , see Fig. 5.1. The Z values for each site are chosen between $Z_{min} = -0.75 \text{ \AA}$ (below the surface Al atom by $0.75 \text{ \AA}$) and $Z_{max} = 7.50 \text{ \AA}$ with a step of $0.25 \text{ \AA}$ (a total of 34 values of Z were used). The 1D reference potential $Q^{1D}(R_i)$ is obtained from this DFT data set for site 1 through a cubic spline interpolation, imposing the condition $Q^{1D}(R_i) = 0$ and $dQ^{1D}/dR_i = 0$ for $R_i > Z_{max}$. The 3D interpolation function I^{3D} is obtained by performing a spline interpolation over Z and then a 2D spline interpolation over the X and Y coordinates [70].

B. H_2 + Ti/Al(100) 6D PES

To construct the 6D interpolation function I^{6D} , first we fix the center of mass (X, Y) coordinates of the H_2 molecule, and its orientation angles (θ, ϕ), and obtain 2D cuts in (Z, r) by interpolating DFT data using 2D cubic splines. Next, for each (X, Y) site the dependence on (θ, ϕ) is described by a Fourier interpolation. Finally, the dependence on the center of mass (COM) coordinates (X, Y) is obtained through an interpolation by 2D cubic splines. The interpolation is based on 44 2D cuts (Z, r):

(1) COM at Site 1, the top Al site ($X = 0, Y = 0$) (see Fig. 5.1), four configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$), ($\theta = \pi/2, \phi = \pi/4$) and ($\theta = \pi/2, \phi = 3\pi/4$).

(2) At Site 2, the bridge site ($X = \Delta/4, Y = 0$), three configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$) and ($\theta = \pi/2, \phi = \pi/2$).

(3) At Site 3, the Ti hollow site ($X = \Delta/4, Y = \Delta/4$), three configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$) and ($\theta = \pi/2, \phi = \pi/4$).

(4) At Site 4, the Al hollow site ($X = 3\Delta/4, Y = \Delta/4$) three configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$) and ($\theta = \pi/2, \phi = \pi/4$).

(5) At Site 5, halfway between the top Al and the bridge sites ($X = \Delta/8, Y = 0$), seven configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$), ($\theta = \pi/2, \phi = \pi/2$), ($\theta = \pi/4, \phi = 0$), ($\theta = \pi/4, \phi = \pi/2$), ($\theta = \pi/4, \phi = \pi$) and ($\theta = \pi/4, \phi = 3\pi/2$).

(6) At Site 6, halfway between the top Al and the hollow Ti sites ($X = \Delta/8, Y = \Delta/8$), six configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = \pi/4$), ($\theta = \pi/2, \phi = 3\pi/4$), ($\theta = \pi/4, \phi = \pi/4$), ($\theta = \pi/4, \phi = 3\pi/4$) and ($\theta = \pi/4, \phi = 5\pi/4$).

(7) At Site 7, halfway between the bridge and the hollow Ti sites ($X = \Delta/4, Y = \Delta/8$), six configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$), ($\theta = \pi/2, \phi = \pi/2$), ($\theta = \pi/4, \phi = 0$), ($\theta = \pi/4, \phi = \pi/2$) and ($\theta = \pi/4, \phi = 3\pi/2$).

(8) At Site 8, halfway between the top Al and the hollow Al sites ($X = 5\Delta/8, Y = \Delta/8$), six configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = \pi/4$), ($\theta = \pi/2, \phi = 3\pi/4$), ($\theta = \pi/4, \phi = \pi/4$), ($\theta = \pi/4, \phi = 3\pi/4$) and ($\theta = \pi/4, \phi = 7\pi/4$).

(9) At Site 9, halfway between the bridge and the hollow Al sites ($X = 3\Delta/4, Y = \Delta/8$), six configurations are calculated: ($\theta = 0$), ($\theta = \pi/2, \phi = 0$), ($\theta = \pi/2, \phi = \pi/2$), ($\theta = \pi/4, \phi = 0$), ($\theta = \pi/4, \phi = \pi/2$) and ($\theta = \pi/4, \phi = 3\pi/2$).

In the above $\Delta = \sqrt{2} \times a$ is the size of the (2×2) unit cell (see Fig. 5.1). The tilted molecular configurations, *i.e.*, with $\theta = \pi/4$, which are also calculated on the low symmetry sites (like the point in the middle between the top and fcc sites) are necessary to obtain the required accuracy on the alloyed surface with $c(2 \times 2)$ symmetry.

For each 2D cut in (Z, r) we have calculated DFT data for 13 values of r (0.4, 0.5, 0.6, 0.7, 0.75, 0.8, 0.9, 1.0, 1.25, 1.5, 1.75, 2.0, 2.3 Å), and 26 Z values with equal

spacing between $Z_{min} = 0.25 \text{ \AA}$ and $Z_{max} = 6.50 \text{ \AA}$, with a step of $0.25 \text{ \AA}$. The distribution of the points is denser in the entrance channel to avoid artificial corrugation and increase the precision in this region, which is the most important for the dynamics [72].

5.2.3 CT and QCT calculations

In the CT and QCT simulations, the projections of the initial configurations of the trajectories on the surface are inside the (2×2) unit cell [the large square area by solid lines in Fig. 5.1 (a)], and sampled by the Monte Carlo method. The implementation of the periodic boundary conditions [see Fig. 5.1 (a)] in the PES ensures that translating the molecule from one unit cell to another without changing the relative position of the molecule in the unit cell will not affect the interaction potential. All the initial configurations correspond to H_2 in the gas phase, with $Z = 6.5 \text{ \AA}$ above the surface unit cell, see Fig. 5.1 (b). Several different initial quantum rovibrational states (v, j, m_j) are considered, in which the initial angular momentum is fixed according to $|\mathbf{L}| = \sqrt{j(j+1)}$, and the orientation of the $\mathbf{L}$ vector is selected randomly with the constraint of

$$\cos(\theta_L) = \frac{m_j}{\sqrt{j(j+1)}}, \quad (5.3)$$

where θ_L is the angle between $\mathbf{L}$ and the Z axis (which is perpendicular to the surface), j is the rotational quantum number, and m_j is the magnetic rotational quantum number. The QCT trajectories are propagated by the velocity Verlet scheme [77, 78]. In the CT calculations, the ZPE is not taken into account, whereas the QCT calculations include the initial ZPE. If the final H–H distance is larger than $2.3 \text{ \AA}$, the H_2 molecule is considered to be dissociated. Otherwise, the H_2 molecule is considered to be reflected from the surface to the gas phase when Z exceeds $6.5 \text{ \AA}$ and H_2 has a velocity pointing towards the vacuum. More details of the CT and QCT methods can be found in Chapter 2.6 and 4.2.3.

The reaction probability in the micro-canonical ensemble is calculated as the ratio of the number of dissociated trajectories and the total number of trajectories run.

5.2.4 Effective barrier heights and rovibrational efficacies in QCT calculations

For molecule–metal surface systems, the state-resolved reaction probability $R(v, j; E_{kin})$ can often be fitted to the expression [79, 80],

$$R(v, j; E_{kin}) = \frac{A(v, j)}{2} \left\{ 1 + \operatorname{erf} \left(\frac{E_{kin} - E_0(v, j)}{W(v, j)} \right) \right\}, \quad (5.4)$$

where $A(v, j)$ is a global scaling factor (≤ 1) that establishes the asymptotic (saturation, maximum) value of $R(v, j; E_{kin})$, $E_0(v, j)$ is the collision energy corresponding to half the saturation value, and $W(v, j)$ is the width parameter that controls the steepness of the error function $\text{erf}()$. In order to study the stereodynamic effect of the initial rovibrational state on the reactivity for a fixed slab model, we also define an effective barrier height $E_0(v, j, m_j)$ as the collision energy at which the state-resolved reaction probability $R(v, j, m_j; E_{kin})$ becomes equal to half the saturation value obtained from the QCT calculations.

The vibrational efficacy $\Theta_v(P_r)$ [81, 82], may be calculated from

$$\Theta_v(P_r) = \frac{E_{kin}^{v=0}(P_r) - E_{kin}^{v=1}(P_r)}{E_{vib}(v=1) - E_{vib}(v=0)}. \quad (5.5)$$

Here, E_{kin}^v is the translational energy required to obtain a reaction probability P_r with H_2 initially in the vibrational state v . An efficacy value of $\Theta_v(P_r)$ larger than 1.0 means that putting energy into vibration is more efficient at promoting reaction than putting energy into translation. The opposite is true for a value less than 1.0. Rotational efficacy may be obtained in a similar way, as further discussed below in the Section 5.3.

To test the accuracy of the QCT method, the quantum effect should be considered by comparison with QD calculations. Thus, the calculation of the H_2 dissociation probabilities by the TDWP method is considered in the next subsection.

5.2.5 TDWP calculations

In our implementation of 6D quantum dynamics [42, 83], we use the same method as has been introduced in our previous paper of $H_2 + 1$ ML Ti/Al(100) system [26]. The 6D Hamiltonian operator including the translational, vibrational, rotational and potential energy terms is given by

$$\hat{H}_{6D} = -\frac{1}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu r^2} + V_{6D}(X, Y, Z, r, \theta, \phi). \quad (5.6)$$

In Eq. 5.6, μ is the reduced mass associated with the vibrational motion of H_2 . V_{6D} is the 6D CRP PES, computed by the interpolation described in Section 5.2.2. The split-operator (SPO) method [84] is used to propagate the wave packet.

Only normal incidence is considered in this paper. For each PES (based on the PW91 and RPBE functionals respectively), two initial wave packets with H_2 in its rovibrational ground state and first vibrationally excited state are propagated to obtain results in the kinetic energy ranges of 0.40 – 1.0 eV (for the rovibrational ground state) and 0.20 – 1.0 eV (for the vibrationally excited state). The converged SPO time step is 4.0 a.u.

Table 5.2: Parameters used for 6D quantum dynamics for the initial rovibrational ground state ($v = 0, j = 0, m_j = 0$) wave packet and initial vibrational excited state ($v = 1, j = 0, m_j = 0$) wave packet. Both distance and time are in atomic unit (a.u.), and energies are in eV, unless indicated otherwise.

Initial state(v, j, m_j)	(0, 0, 0)	(1, 0, 0)
Parameters	400 – 1000 meV	200 – 1000 meV
Initial wave packet		
Center Z_0	15.0	15.0
v	0	1
j	0	0
m_j	0	0
Propagation time step	4.0	4.0
Total propagation time t	11 000	20 000
Scattering grid		
Range of Z Fourier grid	[0, 19.05]	[0, 19.05]
Grid spacing in Z	0.15	0.15
Range of Z optical potential	[12.15, 19.05]	[12.15, 19.05]
Strength of Z optical potential	0.005	0.005
Range of r Fourier grid	[0.40, 8.20]	[0.40, 8.20]
Grid spacing in r	0.20	0.20
Range of r optical potential	[4.2, 8.2]	[4.2, 8.2]
Strength of r optical potential	0.008	0.008
Range of X (Y) Fourier grid	[0, 7.63]	[0, 7.63]
Grid spacing X (Y)	0.195	0.195
Specular grid		
Range of Z Fourier grid	[0, 28.65]	[0, 22.95]
Grid spacing in Z	0.15	0.15
Range of Z optical potential	[18.0, 28.0]	[18.0, 28.0]
Strength of Z optical potential	0.008	0.008
Rotational basis set		
Maximum j in rotational basis	20	20
Maximum m_j in rotational basis	18	18
Analysis		
Z_∞	12.15	12.15

(0.096 femtosecond). More computational details are listed in Table 5.2, and the TDWP and SPO methods used are described fully in Ref.[42] and Chapter 2.7.

The potential energy and the wave packet are defined on the same grid. The wave function on X , Y , Z , and r is represented by the discrete variable representation (DVR), effectively using a plane-wave basis-set [85, 86]. The angular momentum part of the wave function is represented by a finite basis representation (FBR), using orthogonal normal-

ized associated Legendre polynomials as basis functions. Gauss-Legendre and Fourier transformations are used to transform the wave function from the FBR to the DVR and back [87, 88]. Quadratic optical potentials [89] are employed with strength parameters such that the reflection from and transmission through the optical potential is minimal.

Finally, the wave packet is asymptotically analyzed by the Balint-Kurti formalism [90–93], in which the scattered wave packet is projected at $Z = Z_\infty$ onto the free molecular states. The scattering probability at an incident energy E_{kin} for a transition from the initial state to the final state can be obtained from the S-matrix by

$$P_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin}) = |S_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin})|^2. \quad (5.7)$$

The reaction probability at an incident energy E_{kin} is given by summing up all the scattering probabilities and subtracting from 1,

$$P_r(E_{kin}) = 1 - \sum_{v'j'm'_jnm} P_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin}). \quad (5.8)$$

5.2.6 Molecular beam simulations

In experimental studies of H_2 dissociation on surfaces, supersonic molecular beams are often employed [48, 79, 80] in which H_2 molecules are in a Boltzmann rovibrational state population with a distribution of incidence energies. Thus different rovibrational states and the distribution of the collision energies should be considered.

In the H_2 molecular beam (MB) experiments [48, 79, 80] the averaged collision energy (E_{kin}) depends on the nozzle temperature (T_n) with $E_{kin} \approx 2.5 k_B T_n - 2.7 k_B T_n$, vibrational energy $E_{vib} = k_B T_n$, and a rotational energy $E_{rot} \approx 0.8 k_B T_n$ [80, 94]. The distribution of the velocity $\mathcal{V}_z$ in the MB for various nozzle temperatures can be obtained from time-of-flight mass spectrometry, and obeys [48, 80, 95],

$$f(\mathcal{V}_z; T_n) = C \mathcal{V}_z^3 e^{-\frac{(\mathcal{V}_z - \mathcal{V}_0)^2}{\alpha^2}}, \quad (5.9)$$

where C is a constant, $\mathcal{V}_0$ is the nozzle temperature dependent stream velocity, and α is the width of the velocity distribution. The Boltzmann factor of a rovibrational state (v, j) in the MB can be given by,

$$F_B(v, j, T_n) = e^{-\frac{E_{vib}(v)}{k_B T_n}} w(j) (2j + 1) e^{-\frac{E_{rot}^v(j)}{0.8 k_B T_n}} / N, \quad (5.10)$$

where $w(j)$ is a weight function for H_2 nuclear spin statistics. $w(j) = 1$ for even j values and $w(j) = 3$ for odd j . N is the normalization factor,

$$N = \sum_{v,j} e^{-\frac{E_{vib}(v)}{k_B T_n}} w(j) (2j + 1) e^{-\frac{E_{rot}^v(j)}{0.8 k_B T_n}}. \quad (5.11)$$

Thus the energy resolved reaction probability is calculated from,

$$R(E_{kin}; T_n) = \sum_{v,j} F_B(v, j, T_n) R(E_{kin}; v, j), \quad (5.12)$$

where $R(E_{kin}; v, j)$ is the reaction probability from QCT results. The simulated MB reaction probability $R(T_n)$ is equal to the energy-resolved reaction probability $R(E_{kin}; T_n)$ convoluted with the velocity distribution in Eq. 5.9:

$$R(T_n) = \frac{\int_0^\infty f(\mathcal{V}_z; T_n) R(E_{kin}; T_n) d\mathcal{V}_z}{\int_0^\infty f(\mathcal{V}_z; T_n) d\mathcal{V}_z}. \quad (5.13)$$

The maximum velocity used in the integration of Eq. 5.13 is 12400 m/s (or $E_{kin} = 1.60$ eV), and the highest T_n is 1700 K.

5.2.7 H₂ dissociation rate constant calculations by transition state theory and quasi-classical trajectories

A. TST rate constant

In our application of transition state theory to H₂ + Ti/Al(100), the reaction coordinate s is the distance along the minimum energy path (MEP), with $s = 0$ at the saddle point, negative s on the reactant side, and positive s on the product side. The TST rate constant at temperature T is given by [56, 57],

$$k^{TST}(T, s) = \frac{\sigma}{\beta \hbar} \frac{Q^{TST}(T, s)}{Q^R(T)} e^{-\beta V_{MEP}(s)}, \quad (5.14)$$

where σ is the number of symmetry-equivalent reaction paths, $\beta = 1/(k_B T)$ and $\hbar$ is Planck's constant. $Q^R(T)$ is the 6D canonical reactant partition function and $Q^{TST}(T, s)$ is the 5D canonical transition state partition function at s evaluated from the potential energy $V_{MEP}(s)$ along the MEP.

The variational transition state theory (VTST) rate constant k^{VTST} is the one that minimizes the TST rate constant k^{TST} in Eq. 5.14,

$$k^{VTST}(T) = \min_s k^{TST}(T, s). \quad (5.15)$$

More details about TST and VTST can be found in Chapter 2.8.

B. QCT rate constant

The H₂ dissociation rate constant can also be obtained from reaction probabilities computed with the QCT method (see Section 5.2.3). The Ti/Al(100) surface can be imaged

as a wall in contact with H_2 gas. Consider a wall of an area A , and molecules moving towards the wall with normal incidence velocities $\mathcal{V}_z$ (negative direction of Z coordinate). The collision rate $\mathcal{N}_{col}$ (number of collisions per unit area and time) can be given by [45, 96],

$$\mathcal{N}_{col} = \frac{1}{A} \frac{dN_{col}}{dt} = N \int_0^\infty \mathcal{V}_z f(\mathcal{V}_z) d\mathcal{V}_z \quad (5.16)$$

$$= \frac{p}{k_B T} \sqrt{\frac{M}{2\pi k_B T}} \int_0^\infty \mathcal{V}_z e^{-\frac{M\mathcal{V}_z^2}{2k_B T}} d\mathcal{V}_z, \quad (5.17)$$

where N is the number density of the H_2 molecule with $N = p/k_B T$, $f(\mathcal{V}_z)$ is the velocity distribution of the H_2 molecule, and p is the pressure of the system.

The direct dissociation of H_2 can be written as [57],



where Σ is an empty site available for H_2 dissociation and $k = k(T)$ is the rate constant. The rate $\mathcal{R}$ of this reaction is

$$\mathcal{R} = \frac{1}{A} \frac{d\xi}{dt} = k \cdot [H_2(g)] \cdot [\Sigma], \quad (5.19)$$

where $[H_2(g)]$ is the H_2 concentration with $[H_2(g)] = p/k_B T$, $[\Sigma]$ is the empty site coverage and ξ is the number of dissociated H_2 molecules. $[H_2(g)]$ and $[\Sigma]$ have units of (molecule $\cdot m^{-3}$) and (site $\cdot m^{-2}$), respectively. $\mathcal{R}$ can be calculated from Eq. 5.17 by,

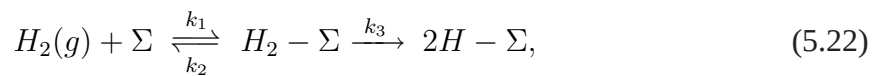
$$\mathcal{R} = \frac{p}{k_B T} \sqrt{\frac{M}{2\pi k_B T}} \int_0^\infty R(\mathcal{V}_z; T) \mathcal{V}_z e^{-\frac{M\mathcal{V}_z^2}{2k_B T}} d\mathcal{V}_z, \quad (5.20)$$

where $R(\mathcal{V}_z; T)$ is the velocity resolved micro-canonical reaction probability, which can be obtained from the energy resolved one $R(E_{kin}; T)$ in Eq. 5.12, through $E_{kin} = M\mathcal{V}_z^2/2$. Because H_2 molecules are presumed to be in the gas phase, the rotational energy E_{rot}^v used in Eq. 5.10 and 5.11 is divided by $k_B T$ rather than $0.8 k_B T_n$ in the MB simulations. Thus, the temperature dependent QCT rate constant $k^{QCT}(T)$ is given by,

$$k^{QCT}(T) = \frac{1}{[\Sigma]} \sqrt{\frac{M}{2\pi k_B T}} \int_0^\infty R(\mathcal{V}_z; T) \mathcal{V}_z e^{-\frac{M\mathcal{V}_z^2}{2k_B T}} d\mathcal{V}_z, \quad (5.21)$$

where $k^{QCT}(T)$ has units of (m³ $\cdot$ site⁻¹ $\cdot$ s⁻¹).

For the 1 ML Ti/Al(100) surface system considered in Ref. [21, 26], there is a molecular adsorption well in front of the barrier. Then, the H_2 dissociation can be regarded as proceeding in two steps,



where $k_i = k_i(T)$ ($i = 1, 2, 3$), k_1 (k_2) are the H_2 forward adsorption (backward desorption) rate constants, and k_3 is the H_2 - Σ dissociation rate constant. Using the steady state approximation [57], $k_1[H_2(g)] \cdot [\Sigma] - k_2[H_2 - \Sigma] - k_3[H_2 - \Sigma] = 0$, the H_2 dissociation rate $\mathcal{R}$ on the 1 ML Ti/Al(100) surface can be given by [57],

$$\mathcal{R} = -\frac{1}{A} \frac{d\xi}{dt} = k_{int}(T)[H_2(g)] \cdot [\Sigma], \quad (5.23)$$

$$k_{int}(T) = \frac{k_1 k_3}{k_2 + k_3} \quad (5.24)$$

where $k_{int}(T)$ is the overall intermediate rate constant under the steady state approximation with unit of ($m^3 \cdot \text{site}^{-1} \cdot s^{-1}$). The $k_{int}(T)$ can be either calculated from the QCT rate constant expression in Eq. 5.21, or from TST (VTST) where k_1 , k_2 and k_3 can be calculated correspondingly from Eq. 5.14 (Eq. 5.15). k_1 has a unit of ($m^3 \cdot \text{site}^{-1} \cdot s^{-1}$). k_2 and k_3 both have the same unit of (s^{-1}).

5.3 Results and discussion

5.3.1 PES obtained from the corrugation reducing procedure

Using the CRP introduced in Section 5.2.2, two 6D PESs are obtained for the PW91 and RPBE functionals, respectively. Two-dimensional (2D) cuts through the PES are shown in Figs. 5.2 and Figs. 5.3. For the PW91 functional, 2D (Z, r) plots (where the other four coordinates X, Y, θ and ϕ are fixed) for H_2 dissociating over the bridge site, the top Al site, the hollow Ti site and the hollow Al site are shown in Figs. 5.2 (a – d) respectively. A 2D (X, Y) plot is shown in Fig. 5.2 (e) corresponding to the barrier H–H distance fixed at $r = 2.09$ bohr and relaxing the Z, θ and ϕ coordinates. The corresponding 2D plots for the RPBE functional are shown in Figs. 5.3 (a – e). The 2D (Z, r) cut in Fig. 5.2 (a) presents a H_2 dissociation barrier height of 0.66 eV, slightly higher than the CINEB result (0.65 eV in Table 5.1) for the PW91 functional (see also Table 5.3). From a relaxation on the CRP PES, we find that the H_2 dissociation has a minimum energy path (MEP) with the COM of the initial configuration at the bridge site and the dissociated H-atoms at the top Al sites as shown in Fig. 5.2 (e), but the COM of the barrier geometry ($X = \Delta/4, Y = 0.32$ bohr) is not exactly at the bridge site, which is in good agreement with the barrier geometry found by employing the CINEB calculations shown in Table 5.1. This shift of the barrier geometry is due to the corrugation of the alloy surface where the hollow Ti site is more attractive to H_2 than the hollow Al site. The RPBE 2D cut barrier height in Fig. 5.3 (a) (0.86 eV) is also slightly higher than the one obtained from CINEB calculations (0.84 eV in Table 5.1, also see Table 5.3).

Although H_2 dissociation from hollow Al sites has higher barrier heights than from

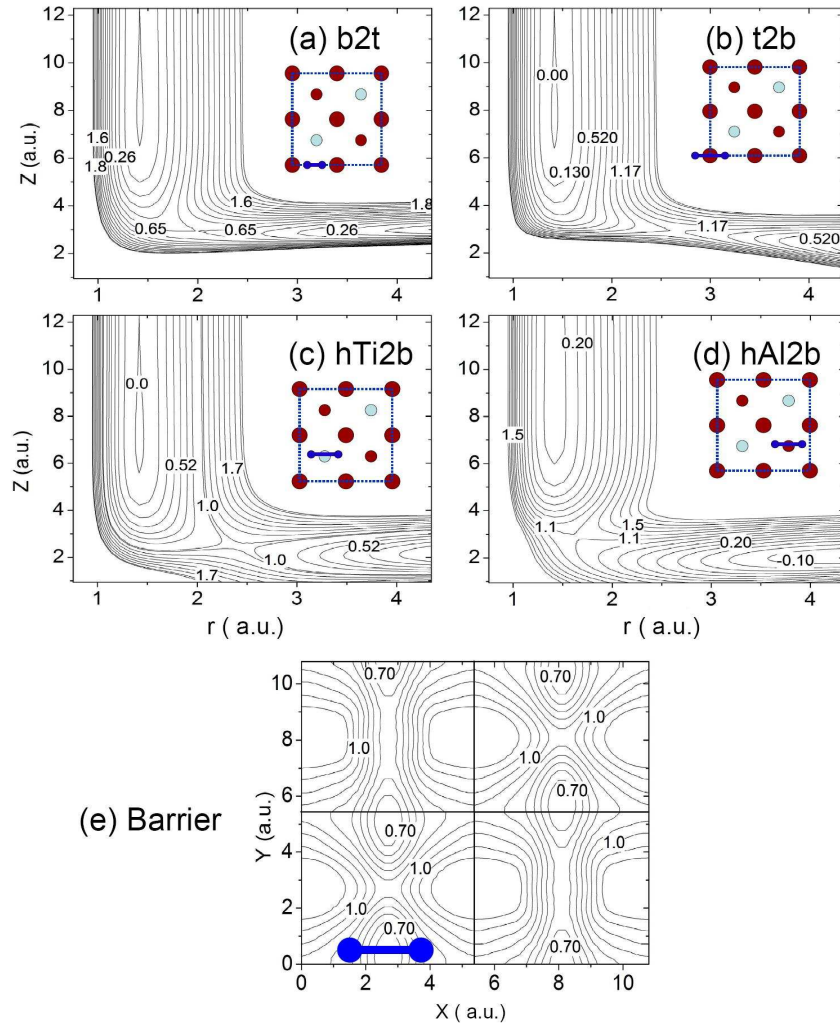


Figure 5.2: PES 2D cuts computed with the PW91 functional. (a) 2D (Z, r) cut with H_2 COM fixed above the bridge site and $\theta = 90^\circ$ and $\phi = 0.0^\circ$, and the dissociated two H-atoms are at the neighboring top Al sites (b2t), where the inset figure illustrates the (2×2) surface unit cell and the initial location of the H_2 geometry; (b) same as (a) but with the COM fixed at the top Al site and the dissociated H-atoms are at the two neighboring bridge sites (t2b); (c) same as (a) but with the COM fixed at the hollow Ti site and the dissociated H-atoms are at the two neighboring bridge sites (hTi2b); (d) same as (a) but with the COM fixed at the hollow Al site and the dissociated H-atoms are at the two neighboring bridge sites (hAl2b). Figure (e) is the 2D cut along (X, Y) when r is fixed at the barrier H-H distance, with relaxation of Z , θ and ϕ , where the inset two H-atoms illustrate the barrier position, with the COM moved along the Y coordinate by 0.32 bohr.

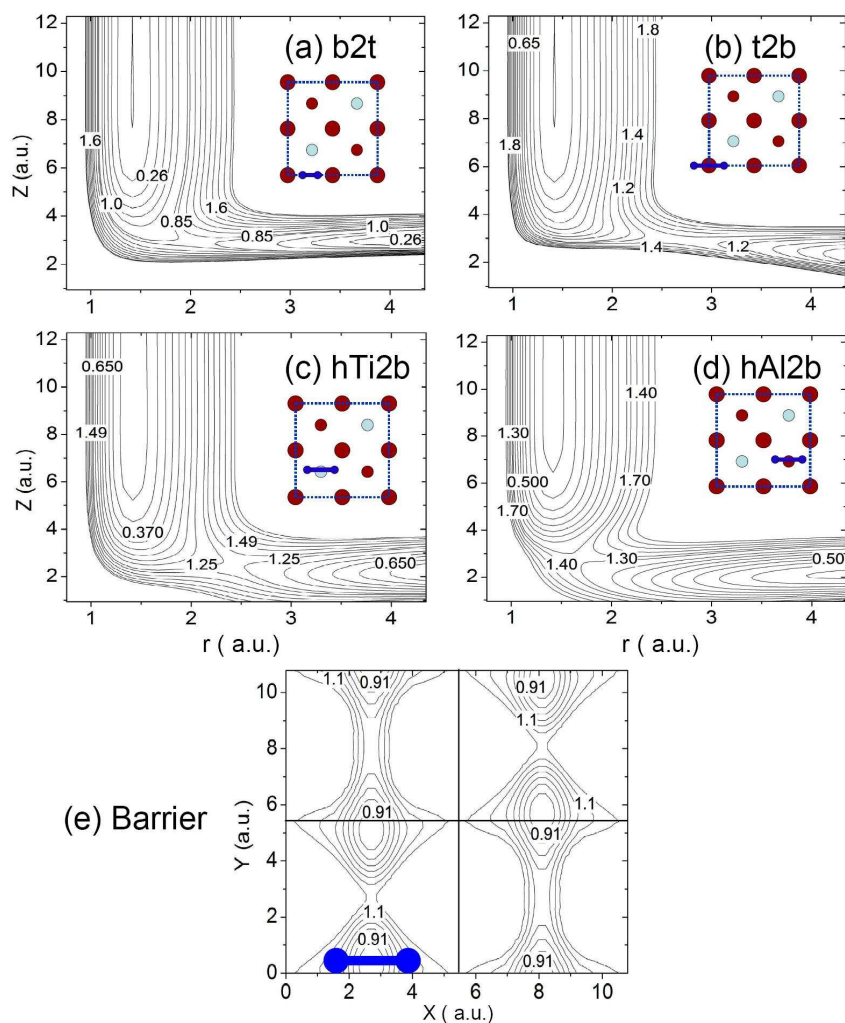


Figure 5.3: Same as Fig. 5.2, but for the RPBE functional.

the hollow Ti site (see Table 5.3), there is an atomic chemisorption well with depth - 0.21 eV in the dissociation path for the PW91 functional [see Fig. 5.2 (d)], with the minimum of the well at an H-H distance of 4.48 bohr (almost fully dissociated to the bridge site). There is no atomic chemisorption well observed for the RPBE functional [see Fig. 5.3 (d)]. Thus, the dissociation chemisorption is exothermic according to the PW91 functional, but endothermic according to the RPBE functional. The details of the barrier heights and geometries corresponding to the 2D cuts in Figs. 5.2 and Figs. 5.3 are given in Table 5.3.

Table 5.3: Barrier heights (E_b , in eV) and barrier geometries (X , Y , Z and r , in bohr, in which $\theta = 90^\circ$ and $\phi = 0.0^\circ$ are fixed) obtained from the 2D cuts and relaxations (MEP barrier) of the CRP PESs, which are shown in Fig. 5.2 and Fig. 5.3 for the PW91 and RPBE functionals, respectively. The labels b2t, t2b, hTi2b and hAl2b represent the same cuts as in the figures.

2D cuts	E_b	X	Y	Z	r
PW91 functional					
b2t	0.66	$\Delta/4$	0	2.93	1.96
t2b	1.17	0	0	2.93	2.67
hTi2b	1.03	$\Delta/4$	$\Delta/4$	2.50	2.40
hAl2b	1.12	$3\Delta/4$	$\Delta/4$	2.82	1.63
MEP barrier	0.65	$\Delta/4$	0.32	2.90	2.09
RPBE functional					
b2t	0.86	$\Delta/4$	0	2.93	2.02
t2b	1.38	0	0	2.93	2.66
hTi2b	1.26	$\Delta/4$	$\Delta/4$	2.55	2.41
hAl2b	1.32	$3\Delta/4$	$\Delta/4$	2.80	1.67
MEP barrier	0.84	$\Delta/4$	0.31	2.92	2.11

5.3.2 Quasi-classical H_2 dissociation probabilities

For the two PESs constructed from the CRP method with the PW91 and RPBE functionals, 6D quasi-classical dynamical trajectory calculations are performed. Reaction probabilities are obtained for the following H_2 initial rovibrational states: the vibrational ground state for $j = 0$ to $j = 10$, and the vibrationally excited $v = 1$ state for $j = 0$ to $j = 7$ (a total of 185 rovibrational states (v, j, m_j) for both the PW91 and RPBE functionals). For each H_2 initial state, calculations are carried out for 60 incident energies, with equal spacing in the range from 0.03 to 1.60 eV, and for each incident energy 5000 trajectories have been run.

For H_2 -surface systems, the helicopter rotational states ($m_j = j$ with their angular momentum j oriented perpendicular to the surface, in Eq. 5.3) have higher dissociation probabilities than the cartwheel rotational states ($m_j = 0$ with their angular momentum oriented parallel to the surface). To demonstrate this phenomenon, results for the $j = 5$ state are shown in Fig. 5.4 (a–b) for the PW91 and RPBE functionals, respectively. At a nozzle temperature of 1700 K, the population of the ($v = 0, j = 5$) state is about 15.0 % in the molecular beam. The PW91 results for the cartwheel ($j = 5, m_j = 0$) state show a zero reaction probability for collision energies E_{kin} smaller than 0.60 eV, and the RPBE results for E_{kin} smaller than 0.80 eV. This is consistent with the PW91 barrier height being about 0.20 eV lower than the RPBE one. As for most other H_2 -metal systems [26, 35, 40, 97], the reaction probability increases monotonically with m_j , regardless of which functional

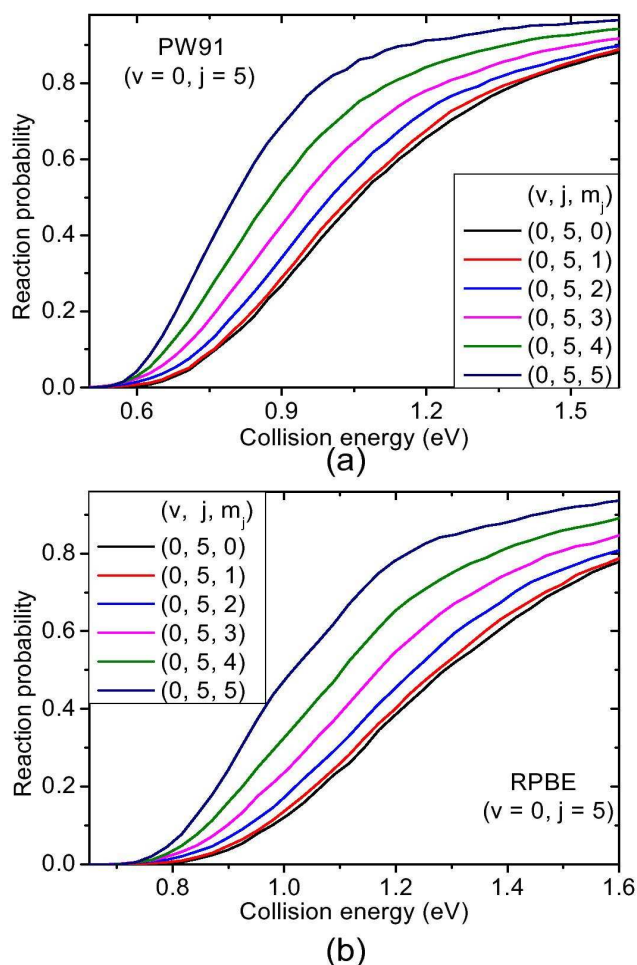


Figure 5.4: (a) Quasi-classical reaction probability of $(v=0, j=5, m_j)$ H_2 , for $m_j = 0 - 5$. The trajectories are run on the PES computed with the PW91 functional. (b) The same as (a) but for the RPBE PES.

is used, see Fig. 5.4 (a – b).

The PW91 degeneracy averaged reaction probability is shown for the $(v=0, j=0)$ to $(v=0, j=10)$ states in Fig. 5.5 (a), and the $(v=1, j=0)$ to $(v=1, j=7)$ states in Fig. 5.6 (a). For $v=0$, the reaction probabilities increase with E_{kin} and have S-shapes for all j states.

For rotational states in the vibrational ground state with $j < 7$, there is no clear trend on how the reaction probability changes with j . At $E_{kin} = 0.80$ eV, the reaction probability of $j=1$ state almost has the same value as that of the $j=0$ state [see Fig. 5.5

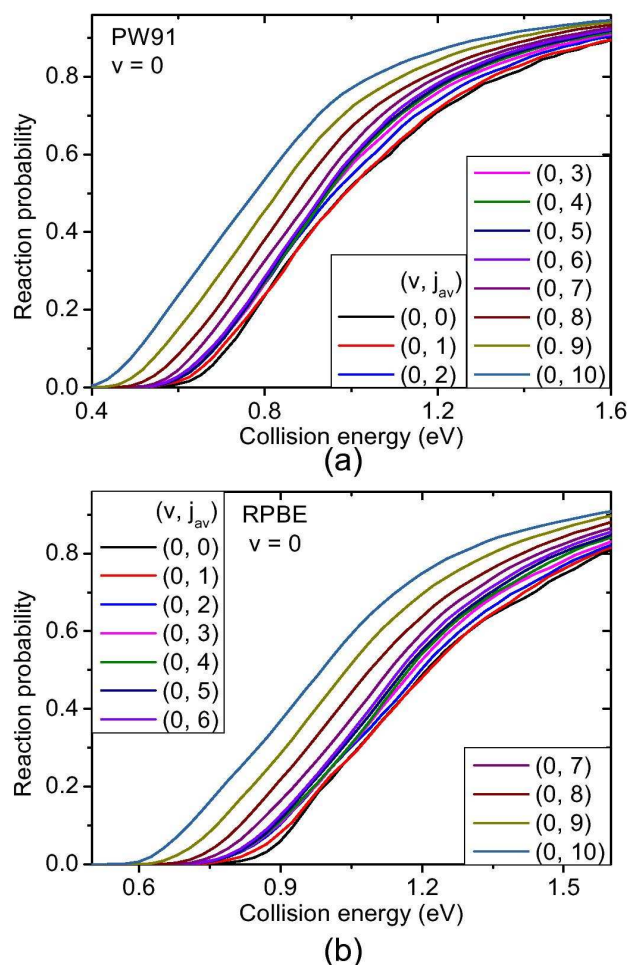


Figure 5.5: (a) Degeneracy averaged reaction probabilities for (v, j) states are shown, as computed with the QCT method using the PW91 functional for $v = 0$. (b) The same as (a) but using the RPBE PES.

(a)]. The reaction probabilities of the $j = 3 - 6$ states almost overlap with each other [see Fig. 5.5 (a)]. The effect is reminiscent of the competition between rotational hindering and rotational enhancement seen for $H_2 + Cu(111)$ [80]. In this latter system, the H_2 molecule also experiences a late activation barrier of 0.60 eV [39]. In our Ti/Al(100) system, rotational excitation only increases the reaction probabilities consistently for $j \geq 7$ [see Fig. 5.5 (a)]. The RPBE results lead to the same conclusions for the effect of j on reaction as shown in Fig. 5.5 (b), except for the shift of the collision energies by 0.2 eV.

For the vibrationally excited states with $j < 7$, the rotational hindering effect is even

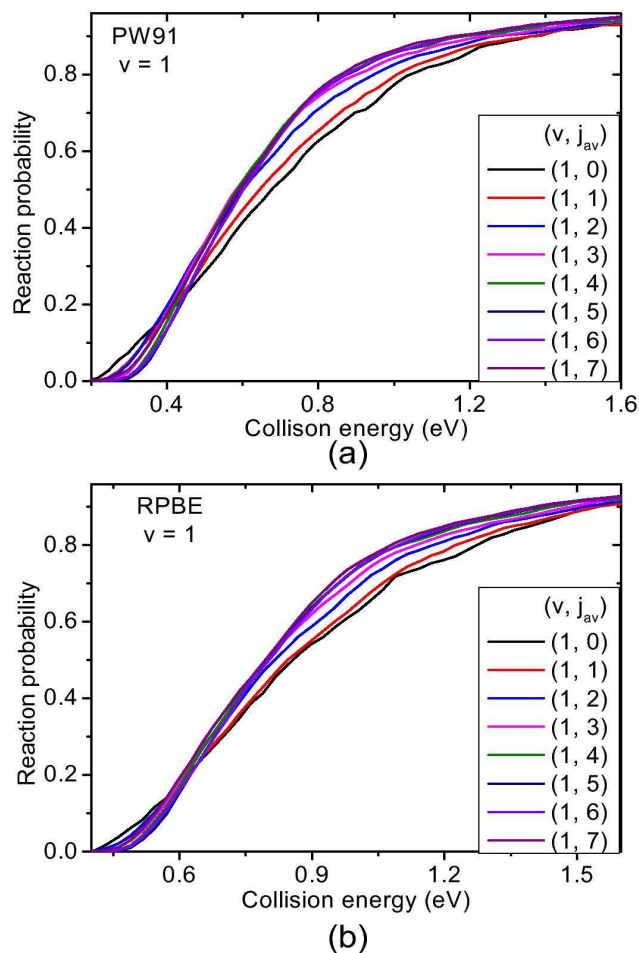


Figure 5.6: (a) Degeneracy averaged reaction probabilities for (v, j) states are shown, as computed with the QCT method using the PW91 functional for $v = 1$. (b) The same as (a) but using the RPBE PES.

more important, as can be observed for reaction probabilities $< 10.0\%$, see Fig. 5.6 (a – b) for both functionals.

At a quantum level of detail, we find that for $v = 0$, the reaction probabilities of helicopter rotational states increase monotonically with j , except around $E_{kin} = 0.60$ eV where the $(j = m_j = 3 - 6)$ states have almost the same reaction probability of 5.0% [see Fig. 5.7 (a)]. However, the hindering effect is especially significant in the cartwheel states. The $j = 6 - 8$ cartwheel states show a lower reactivity than the $j = 0$ state at low incidence energies [see Fig. 5.7 (b)]. When j is greater than 7, the reaction probability

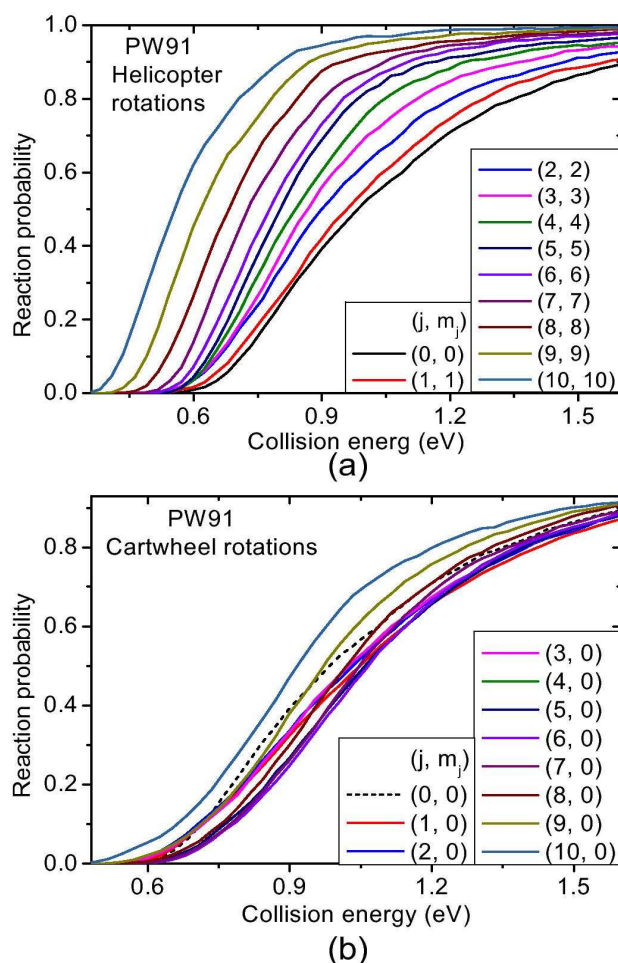


Figure 5.7: (a) Quasi-classical reaction probabilities for $v = 0$, $j = 0 - 10$ and $m_j = j$ (helicopter rotation state) are shown, using the PW91 PES. (b) The same as (a) but for the $m_j = 0$ (cartwheel rotation state).

monotonically increases with j at high incidence energy.

5.3.3 Stereodynamic effects and rovibrational efficacies from the QCT calculations

To provide a quantitative discussion of the stereodynamic effect of the initial rotational state of H_2 on its reactivity, the effective barriers $E_0(v, j, m_j)$ are calculated (Eq. 5.4 with $A(v, j) = 1.0$ as the maximum value of the reaction probability) for the degeneracy

averaged reaction probabilities of (v, j) states, the helicopter $(j, m_j = j)$ states and the cartwheel $(j, m_j = 0)$ states. They are shown in Fig. 5.8 (a – b) for the PW91 and the RPBE functionals, respectively.

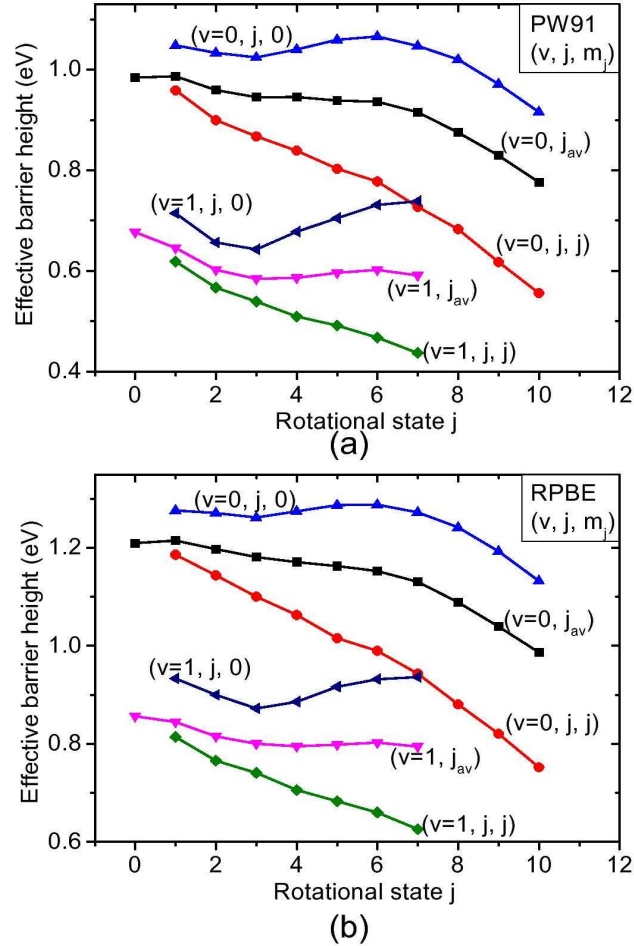


Figure 5.8: (a) The PW91 effective barrier height $E_0(v, j, m_j)$ calculated from Eq. 5.4 for the averaged reaction probabilities of j states, helicopter $(j, m_j = j)$ states and cartwheel $(j, m_j = 0)$ states are considered. (b) The same as (a) but from the RPBE functional.

For the vibrational ground state, the $E_0(v, j)$ (effective barrier) values associated with the degeneracy averaged reaction probabilities are all higher than the DFT barrier height along the MEP (0.65 eV for the PW91 functional and 0.84 eV for the RPBE functional in Table 5.1). This indicates that to reach a reaction probability of $A(v, j)/2$ (see Eq. 5.4), the quasi-classical trajectories in many cases follow higher energy paths, *i.e.*,

H_2 dissociates also at the top Al site. From the PW91 functional results in Fig. 5.8 (a), the degeneracy averaged $E_0(v, j_{av})$ values decrease from 0.98 eV at $j = 0$ to 0.77 eV at $j = 10$, while the effective barrier heights of the $j = 1 - 7$ states are the same to within 0.10 eV, which corresponds to the H_2 dissociation probabilities being close to each other for these states as discussed above in Section 5.3.2. If the two extreme initial rotational states, helicopter and cartwheel, are considered, one can see again that cartwheel states have larger $E_0(v, j, m_j)$ values [see both the PW91 and RPBE results in Fig. 5.8 (a, b)]. The $E_0(v, j, m_j)$ value decreases continuously with increasing j for the helicopter rotational states ($j, m_j = j$). However, the cartwheel state $E_0(v, j, 0)$ value decreases with j from the ($j = 1, m_j = 0$) state to the ($j = 3, m_j = 0$) state and increases to a maximum value of 1.06 eV for the ($j = 6, m_j = 0$) state. Thus, ($j = 6, m_j = 0$) state experiences the highest effective barrier and it is the dynamically most unfavorable initial state for H_2 dissociation. Moreover, the difference between the $E_0(v, j, m_j)$ of cartwheel and helicopter states increases from 0.09 eV at $j = 1$ to 0.36 eV at $j = 10$. The RPBE functional shows similar results as the PW91 ones, except that there is an energy shift of 0.20 eV to the higher energy range.

For $v = 1$ states, employing the PW91 functional, the $E_0(v, j)$ values of degeneracy averaged reaction probabilities decrease from 0.67 eV at $j = 0$ to 0.58 eV at $j = 3$, then keep almost the same value of 0.60 eV until $j = 7$ [see Fig. 5.8 (a)]. The cartwheel rovibrational state ($v = 1, j = 3, m_j = 0$) shows a minimum effective barrier of 0.64 eV and 0.87 eV, for the PW91 and RPBE functionals, respectively. The effective barrier gap between cartwheel and helicopter rovibrational states increases from 0.10 eV for $j = 1$ to 0.30 eV for $j = 7$ for both functionals. The results show that vibrational excitation from $v = 0$ to 1 can lower the effective barrier by about 0.31 eV.

Using the formulae in Eq. 5.5, the vibrational efficacy can be obtained from the reaction probability curves in Fig. 5.5, and Fig. 5.6 [the curves are fitted by Eq. 5.4 with $A(v, j) = 1.0$]. At a typical reaction probability of 50.0 % (half the saturation reaction probability), we obtain vibrational efficacies $\Theta_v(P_r) = 0.61$ for both the PW91 and RPBE functionals, indicating that translational energy is approximately 40 % more effective than the vibrational energy at promoting reaction. The rotational efficacies $\Theta_r(P_r)$ can be obtained similarly to $\Theta_v(P_r)$. Only high j states have enough rotational coupling to the reaction coordinate to have a significant influence on the reaction probability [79]. We calculate the $\Theta_r(P_r)$ from a linear fitting of the effective barrier heights $E_0(v, j)$ of the degeneracy averaged reaction probabilities for $v = 0, j \geq 6$ states, see Fig. 5.9. The slopes yield the $v = 0$ state rotational efficacies 0.35 for both the PW91 and RPBE functionals. In other words, for the high j states, the translational energy is about three times more effective than the rotational energy at promoting reaction. Since the high j states with $v = 1$ have ignorable population densities (less than 0.20 % for $j > 7$ states in the molecular beam at a nozzle temperature of 1700 K), $\Theta_r(P_r)$ for $v = 1$ is not considered here.

H_2 dissociation has a steric preference for dissociation with helicopter rotation

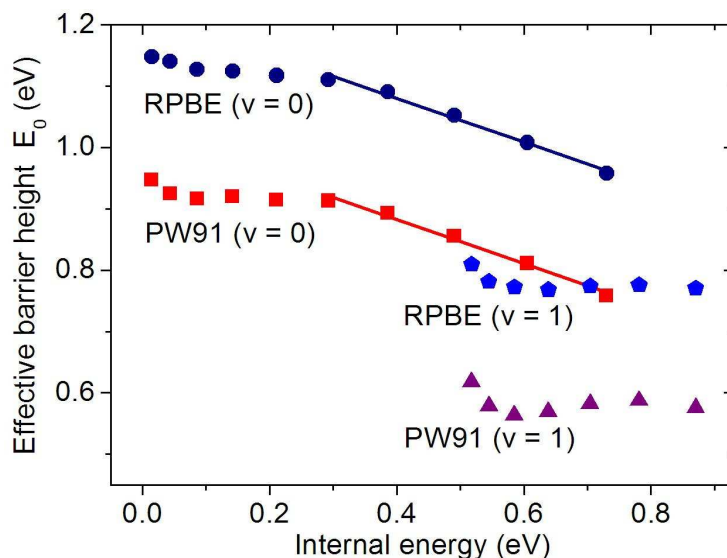


Figure 5.9: Dependence of the effective barrier height $E_0(v, j, m_j)$ calculated from Eq. 5.4 on the internal energy (rotational and vibrational excitation energy) for the PW91 and RPBE functionals, respectively. The lines represent linear fits to the points for high rotational states ($v = 0$) for the PW91 and RPBE functionals.

rather than in the tilted geometries sampled by cartwheel rotational states. In principle, H_2 molecules approaching a surface in an unfavorable orientation can be realigned by the anisotropic interaction potential [98], which is often called the *steering effect*. When the steering is strong, the reaction probability should not depend on the value of m_j . In the case of the 1 ML Ti/Al(100) surface we studied previously [26], the deep molecular adsorption well in front of the barrier caused a strong steering effect in which the reaction probability was independent of m_j . Obviously, for the 1/2 ML Ti/Al(100) surface, the strong dependence of the reaction on molecular orientation indicates that the steering effect does not play such an important role in this system.

5.3.4 Quantum dynamics of H_2 dissociation

Based on the two CRP PESs we built, 6D QD calculations have been performed for normal incidence of H_2 in its ($v = 0, j = 0$) and ($v = 1, j = 0$) states.

The TDWP reaction probability is plotted in Fig. 5.10 (a–b). Corresponding quasi-classical and pure classical reaction probabilities (the latter ones without ZPE) are also shown in this figure. The figures show that the QD calculations are reproduced well by the quasi-classical ones in the whole energy range. For both PESs, the quantum reaction probability of the ($v = 0, j = 0$) state is slightly higher than the QCT one by about 0.02 in

the low energy (0.40 – 0.75 eV for the PW91 PES and 0.60 – 0.95 eV for the RPBE PES). Especially for the PW91 PES, the reaction probability almost overlaps with the QCT one for $E_{kin} > 0.75$ eV, see Fig. 5.10 (a). For ($v = 1, j = 0$), the quantum reaction probability is lower at low energies (0.20 – 0.38 eV for PW91 PES and 0.40 – 0.60 eV for RPBE PES), but somewhat higher than the QCT result at high energies, by about 2.0 %. The overall agreement between the QCT and QD results is very good.

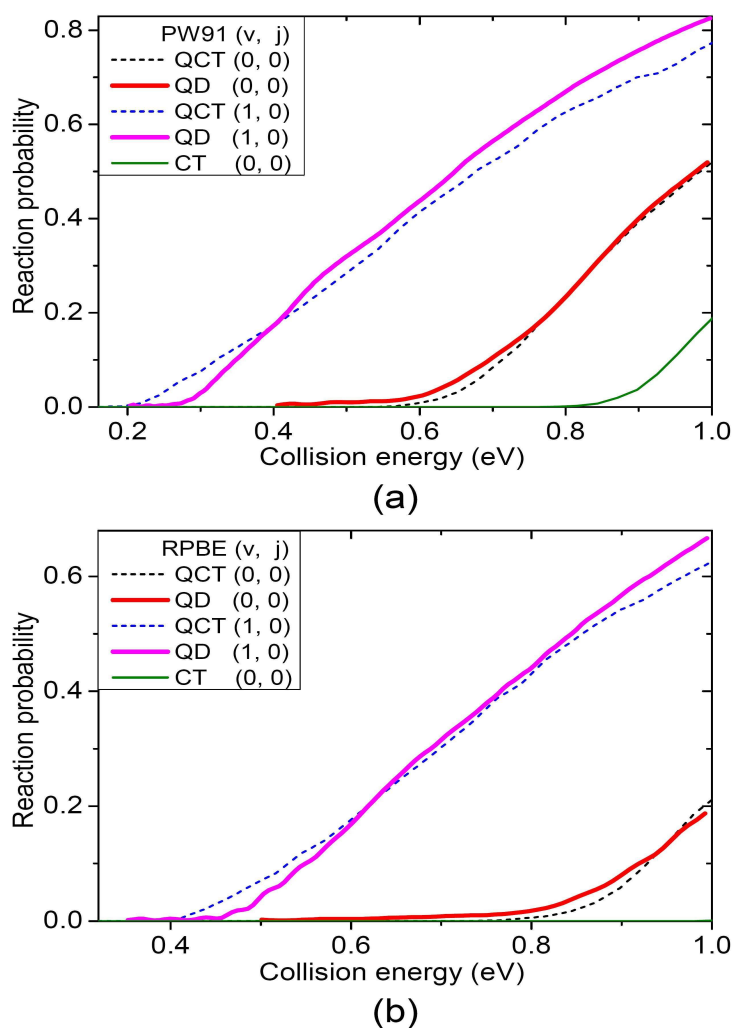


Figure 5.10: (a) The PW91 QD reaction probability for H_2 initially in its ground rovibrational state ($v = 0, j = 0$) and first vibrationally excited state ($v = 1, j = 0$), are shown in solid bold lines. The quasi-classical (in short dashed lines) and the pure classical results (solid green line) are also plotted in a solid line. (b) The same as (a) but for the RPBE functional.

Since the ZPE is not included in the CT method, the classical dynamics reaction probability is zero when E_{kin} is below 0.84 eV (1.0 eV) for the PW91 (RPBE) PES, see Fig. 5.10 (a) [Fig. 5.10 (b)]. Our CT results confirm previous studies [35, 36] showing that activated dissociation of H_2 on metal surfaces is typically described much better with the QCT than with the CT method.

In the 1 ML system (our previous paper in Ref. [26]), we found somewhat worse agreement between the quantum and quasi-classical reaction probabilities in the whole collision energy range studied, $E_{kin} < 0.85$ eV (see Fig. 9 in Ref. [26]). This disagreement was caused by the adsorption well in the PES of the 1 ML system, which makes the H_2 dissociation an indirect (and slow) process, mediated by resonances, which are better described by the quantum method. The peaks exhibited by the quantum reaction probability in the whole collision energy range studied for this system, $E_{kin} < 0.85$ eV, are signatures of such resonances.

In the 1/2 ML system, on the other hand, the quantum and quasi-classical reaction probabilities agree quite well (see Fig. 5.10). In this case, since there is no molecular adsorption well in the PES, only a barrier, the H_2 dissociation is a direct (and fast) process, and is well described by the QCT method. The vibrational excitation probability is very small (less than 0.1 % observed on the scattering grid) and the quantum reaction probabilities are smooth curves, with no peaks, which is a characteristic feature of direct processes.

The good agreement between QD and QCT results suggests that the QCT state-resolved reaction probabilities for other rovibrational states should also be reliable.

5.3.5 Molecular beam simulations results

In the MB simulations, the following H_2 rovibrational states are considered: vibrational ground state $v = 0$ for $j = 0 - 10$, vibrationally excited state $v = 1$ for $j = 0 - 7$. We present results for typical H_2 beams in the same initial conditions as in the experiments by Groot *et al.* [95]. The parameters we employed are summarized in Table 5.4. The results may be viewed as predictions for molecular beam experiments employing H_2 beams of similar characteristics as employed by Groot *et al.* [95].

The MB simulation results are presented in Fig. 5.11. From this figure, we can see that for a nozzle temperature of 1100 K or an average kinetic energy $\langle E_{kin} \rangle = 0.31$ eV, the H_2 dissociation probabilities for both the PW91 and the RPBE functionals are less than 1.0 %. When the nozzle temperature is raised to 1700 K ($\langle E_{kin} \rangle = 0.49$ eV), we find a probability of 6.9 % for the PW91 functional and 1.8 % for the RPBE functional. In a previous study of the $H_2 + Cu(111)$ system [39, 40], the convoluted reaction probabilities were found to be strongly dependent on the experimental beam conditions. Lower reaction probabilities would be obtained using narrower velocity distributions in the MB.

Table 5.4: Parameters used for Eq. 5.9. T_n is the nozzle temperature. $\mathcal{V}_0$ is the T_n dependent stream velocity. α is the T_n dependent width of the distribution. $\langle E_{kin} \rangle$ is the average H_2 kinetic energy with $\langle E_{kin} \rangle = \int_0^\infty E_{kin} f(\mathcal{V}_z; T_n) d\mathcal{V}_z / \int_0^\infty f(\mathcal{V}_z; T_n) d\mathcal{V}_z$, where $f(\mathcal{V}_z; T_n)$ is the velocity distribution in Eq. 5.9. More details are in Ref. [95].

T_n / K	$\langle E_{kin} \rangle$ / eV	$\mathcal{V}_0$ /(m s ⁻¹)	α /(m s ⁻¹)
300	0.078	2605.77	435.73
500	0.135	3290.97	779.61
700	0.191	3806.42	1052.64
900	0.252	4239.84	1350.84
1100	0.308	4607.69	1567.60
1300	0.376	4920.95	1882.90
1500	0.431	5199.08	2072.09
1700	0.490	5393.76	2332.72

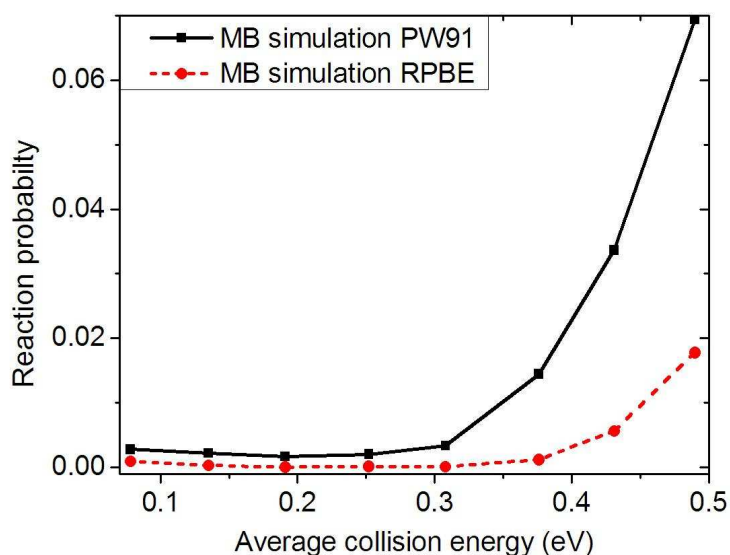


Figure 5.11: Molecular beam simulation using the PW91 and RPBE PESs.

5.3.6 Reaction rate constant calculations by transition state theory and quasi-classical dynamics

Employing TST and VTST, we have calculated the H_2 dissociation rate constants [$k^{TST}(T)$ and $k^{VTST}(T)$] in a range of temperatures (T) 200 K – 1700 K for both slab models, *i.e.*,

1/2 ML and 1 ML Ti/Al(100) surfaces. Only the PW91 rate constants are discussed in this subsection. The $k^{TST}(T)$ and $k^{VTST}(T)$ results are plotted in Fig. 5.12 (a – b). If the molecular adsorption well in the 1 ML Ti/Al(100) surface is not considered, this surface model gives a TST dissociation rate constant $k^{TST}(300K) = 6.00 \times 10^{-14} \text{ cm}^3 \cdot \text{site}^{-1} \cdot \text{s}^{-1}$, which is much larger than the value for 1/2 ML Ti/Al(100) surface, $7.21 \times 10^{-22} \text{ cm}^3 \cdot \text{site}^{-1} \cdot \text{s}^{-1}$. This trend is expected because the activation energy barrier of the 1 ML system (0.15 eV) is much lower than the one in 1/2 ML system (0.65 eV). At 425 K, close to the operating temperature for hydrogen dissociation, the TST rate constants are $2.58 \times 10^{-13} \text{ cm}^3 \cdot \text{site}^{-1} \cdot \text{s}^{-1}$ and $1.32 \times 10^{-19} \text{ cm}^3 \cdot \text{site}^{-1} \cdot \text{s}^{-1}$ for the 1 ML and 1/2 ML Ti-covered surfaces, respectively (see Table 5.5). Due to the minimization of k^{VTST} from k^{TST} (see Eq. 5.15), the rate constants obtained from k^{VTST} are slightly smaller than k^{TST} (see Fig. 5.12).

The QCT rate constants k^{QCT} calculated from Eq. 5.21 are also shown in Fig. 5.12, in which the QCT reaction probabilities are obtained from the Boltzmann average of Eq. 5.12. The empty site coverage $[\Sigma]$ in Eq. 5.19 can be calculated from the lattice constant a of fcc Al with $[\Sigma] = 1/a^2$ (number of site per unit area for square unit cell). Thus, for both 1/2 ML and 1 ML Ti/Al(100) systems, $[\Sigma]$ has the same value, $6.12 \times 10^{14} \text{ site} \cdot \text{cm}^2$. The same rovibrational states are considered as in the molecular beam simulations (see Section 5.3.5). Note that it is unnecessary to calculate the reaction probabilities for all rovibrational states of the 1 ML Ti/Al(100) surface. Due to the fact that the rovibrational efficacies are close to 1.0 [26], the reaction probability of a rovibrationally excited state can be calculated from the ($v = 0, j = 0$) state with a shift of the probability according to the rovibrational energy. For the 1/2 ML Ti-covered system, the k^{QCT} is about 1 order of magnitude larger than the k^{TST} and k^{VTST} results in the entire temperature range. The rate constant is probably overestimated by the QCT results due to rovibrational energy leakage and the nonconservation of the quantization during the dynamics. For the 1 ML Ti-covered system, the k^{QCT} results are significant higher than the TST and VTST ones in the low temperature range (two order of magnitude larger at $T = 200 \text{ K}$), but close to the TST and VTST ones at high temperatures (see Fig. 5.12 and Table 5.5).

If the effect of the intermediate state of the molecular adsorption well in the 1 ML Ti-covered system is considered, the overall rate constant $k_{int}(T)$ in Eq. 5.24 can be calculated. In our implementation, the H_2 molecular adsorption rate constant k_1 is calculated from Eq. 5.21 with the assumption that all collisions are molecular adsorbed ($R(\mathcal{V}_z; T) = 1.0$),

$$k_1 = a^2 \sqrt{\frac{M}{2\pi k_B T}} \int_0^\infty \mathcal{V}_z e^{-\frac{M \mathcal{V}_z^2}{2k_B T}} d\mathcal{V}_z = a^2 \sqrt{\frac{k_B T}{2\pi M}}, \quad (5.25)$$

which indicates that k_1 is proportional to $\sqrt{T}$. k_2 is calculated from TST or VTST, with the initial configuration at the H_2 molecular adsorption well and the barrier height being relative to the gas phase configuration with a value of 0.43 eV. Meanwhile, k_3 is the

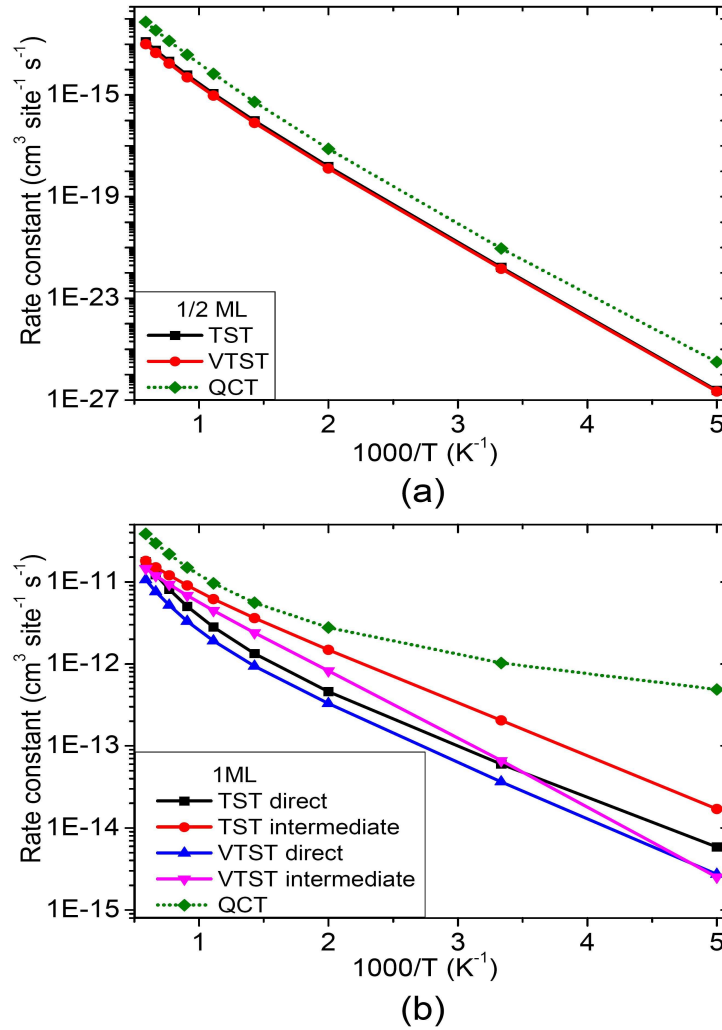


Figure 5.12: H_2 dissociation rate coefficients computed with the TST, VTST (solid lines) and QCT (dotted lines) methods as a function of temperature using the PW91 functional, for both the 1/2 ML (a) and the 1 ML Ti/Al(100) (b) surfaces. The overall steady-state rate coefficient of H_2 dissociation through the intermediate state $H_2-\Sigma$ are also shown for the 1 ML Ti-covered surface.

molecular adsorbed H_2 dissociation rate constant from the initial configuration at the H_2 molecular adsorption well, and the barrier height is 0.58 eV (the barrier is the same as the one in the MEP). Thus, the overall rate constants $k_{int}^{TST}(T)$ ($k_{int}^{VTST}(T)$) considering the intermediate state can be obtained from Eq. 5.24. The results are shown in Fig. 5.12 and Table 5.5. At $T = 425$ K, k_{int}^{TST} (k_{int}^{VTST}) is about three (two) times larger than the k^{TST} (k^{VTST}) value (see Table 5.5), not considering the effect of the well in the latter cases. At high temperature $T = 1700$ K, k_{int}^{TST} (k_{int}^{VTST}) is very close to the k^{TST} (k^{VTST}) results

(see Fig. 5.12 and Table 5.5), which indicates that the trapping of the H_2 in the molecular adsorption well at low temperature is more important than at high temperature.

Table 5.5: At the operating temperatures of dehydrogenation and rehydrogenation, TST (VTST) rate constants k_{TST} (k^{VTST}) calculated from the direct dissociation mechanism of Eq. 5.18, and QCT rate constants k^{QCT} calculated from Eq. 5.21 for H_2 dissociation on both the 1/2 ML and 1 ML Ti/Al(100) surfaces are shown. For the 1 ML Ti-covered system with a molecular adsorption well, the H_2 dissociation TST (VTST) rate constants k_{int}^{TST} (k_{int}^{VTST}) considering the intermediate state are also presented Eq. 5.24. All rate constants have units of $(\text{cm}^3 \cdot \text{site}^{-1} \cdot \text{s}^{-1})$.

Slab Model	Temperature (K)	k^{TST}	k^{VTST}	k^{QCT}	k_{int}^{TST}	k_{int}^{VTST}
1/2 ML	323	8.29 (-22)	7.21 (-22)	4.32 (-21)		
	425	1.32 (-19)	1.12 (-19)	6.36 (-19)		
	1700	1.26 (-13)	1.01 (-13)	7.05 (-13)		
1 ML	323	8.45 (-14)	5.36 (-14)	1.17 (-12)	2.90 (-13)	1.04 (-13)
	425	2.58 (-13)	1.85 (-13)	2.01 (-12)	8.72 (-13)	4.26 (-13)
	1700	1.76 (-11)	1.06 (-11)	3.83 (-11)	1.80 (-11)	1.45 (-11)

The barrier to dissociation referenced to the molecular chemisorption well is about 3.8 times larger than the barrier referenced to the gas phase. However, the rate constants calculated from Eq. 5.14 and Eq. 5.15 also depend on the prefactor of the reactant and transition state partition functions, e.g., $Q^R(T) = \prod_{i=1}^6 1/(1 - e^{-hcv_i/k_B T})$, where v_i is the vibrational frequency of an eigen mode i and c is the speed of light. The prefactor relates to how often a system attempts to undergo the reaction [99]. Because the H_2 –surface antisymmetric stretching (or the hindered cartwheel rotation) and the H_2 –surface symmetric stretching modes all have frequencies (1318 cm^{-1} and 787 cm^{-1} , respectively calculated by numerical centered finite differences) at the well position, the prefactor of k_3 is about 23 times larger than the prefactor of the direct dissociation process in k^{TST} and k^{VTST} at 325 K, which can compensate the cost of the larger value of barrier height. In principle, if the barrier height of H_2 dissociation is much larger than the well depth (small vibrational frequencies or small partition function value at the well position), the molecular adsorbed state can be ignored. Otherwise, the partition function contributes a large weight in the prefactor of the intermediate state (the H_2 –surface system is stable and has large vibrational frequencies at the well position), which will promote the intermediate dissociation process. This last scenario is the one that corresponds to our system.

5.4 Conclusions

In this paper we have studied the elementary reaction of H_2 dissociation on a 1/2 ML Al(100) surface. First, the corrugation reducing procedure has been applied to a density functional theory data set to build six-dimensional electronic ground state potential energy

surfaces using the Born-Oppenheimer and static surface approximations. The PW91 and RPBE functionals have been employed to obtain two different PESs. H_2 dissociation probabilities are calculated through the classical trajectory, quasi-classical trajectory, and the time-dependent wave-packet methods. We have also carried out a molecular beam simulation and computed H_2 dissociation rate constants as a function of temperature using transition state theory.

H_2 dissociation on the 1/2 ML Ti/Al(100) surface has an activation barrier of 0.65 eV (0.84 eV) with H_2 dissociating from the bridge to top sites for the PW91 (RPBE) functional.

Through QCT calculations we have obtained the dissociation probabilities for the following quantum states: $v = 0$, $j = 0 - 10$ and $v = 1$, $j = 0 - 7$ for both the PW91 and RPBE functionals. Considering the effective barrier heights we have found that vibrational excitation to $v = 1$ can promote the H_2 dissociation effectively by lowering the effective barriers by about 0.31 eV. The rotational (vibrational) efficacy obtained from the QCT results shows that the translational energy is about 3.0 (1.6) times more effective than the rotational energy of high j states (vibrational energy) at promoting reaction.

The reaction of H_2 in its rovibrational ground state ($v = 0$, $j = 0$) and its vibrationally excited state ($v = 1$, $j = 0$) has also been studied with QD. The calculations show that the QCT method describes the reaction more accurately than the CT method, as found earlier for most H_2 + metal surface systems studied. The QCT H_2 dissociation probabilities are in good agreement with the QD results for collision energies up to 1.0 eV.

H_2 dissociation rate constants have been calculated using the TST, VTST and QCT methods. The QCT rate constants on the 1/2 ML Ti-covered surface are about 10 times higher than the TST and VTST results. In the 1 ML Ti/Al(100) system, we have considered two situations, *i.e.*, H_2 dissociates directly through the barrier, or may be pre-adsorbed in the molecular adsorption well. The overall TST (VTST) rate constants obtained considering the intermediate state are about three (two) times larger than those obtained for the direct dissociation process at the operating temperature of dehydrogenation and rehydrogenation. At high temperatures (over 500 K), it is justified to treat the dissociation dynamics as a direct process and ignore the effect of the molecular adsorption well.

In summary, based on the evidence that Ti plays a role in the process of hydrogen storage in $NaAlH_4$, we theoretically calculated the H_2 dissociation probability on a 1/2 ML Ti/Al(100) surface. We hope that our predictions of the reaction probability curves can be confirmed by molecular beam experiments. The differences in rate constants obtained between the 1/2 ML and 1 ML Ti coverages may be important to modeling the effect of Ti-coverage of Al on hydrogen sorption in $NaAlH_4$.

5.5 References

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Nederlandse samenvatting

Wat is de katalytische rol die titanium speelt in het waterstof-opslagmateriaal NaAlH_4 ? Het doel van dit proefschrift is de ontrafeling van de dynamica van een elementaire reactie: H_2 dissociatie op $\text{Ti}/\text{Al}(100)$ oppervlakken. Deze reactie is niet de snelheidsbepalende stap in de waterstof opslag van NaAlH_4 , maar dit is een belangrijke reactie om atomair waterstof te produceren dat gebruikt kan worden in andere reactiestappen. Om dit doel te bereiken, hebben we een grote reeks van mogelijke “slabmodellen” getest om het $\text{Ti}/\text{Al}(100)$ oppervlak te beschrijven. Wij hebben zorgvuldig voor twee mogelijke “slabmodellen” gekozen aan de hand van de stabiliteit van het “slabmodel” en de hoogte van de reactiebarrière: (1) het 1/2 ML (mono-laag) Ti-bedekte $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ oppervlak met Ti atomen in de tweede laag, (2) het 1 ML Ti-bedekte $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ oppervlak met Ti atomen in de eerste en derde laag. Met gebruik van deze twee “slabmodellen” is het potentiële energie-oppervlak (PES) berekend. De H_2 -dissociatiewaarschijnlijkheid en de snelheidsconstanten worden dan met behulp van de PES berekend. De resultaten suggereren dat het 1 ML Ti-bedekte $c(2 \times 2)$ - $\text{Ti}/\text{Al}(100)$ oppervlak het meest realistische model is voor de H_2 dissociatie op $\text{Ti}/\text{Al}(100)$ oppervlakken die relevant zijn voor het waterstof-opslagmateriaal NaAlH_4 .

In **Hoofdstuk 1** wordt de noodzaak van ons onderzoek duidelijk gemaakt aan de hand van de beperkte voorraad van fossiele brandstoffen en de impact van CO_2 op het wereldwijde klimaat. De belangrijkste methodes van waterstofproductie worden samengevat. Daarna zullen we ons focussen op één van de waterstof-opslagmaterialen, NaAlH_4 , en de relevante aanpak van gas-oppervlak reacties die in dit proefschrift zal worden gebruikt.

Hoofdstuk 2 introduceert de belangrijkste methodologie die wordt gebruikt in dit proefschrift. De Born-Oppenheimer (BO) benadering en de Kohn-Sham vergelijking in dichtheidsfunctionaaltheorie (DFT) zijn essentiële elementen in dit proefschrift om de verschillende potentiële energie-oppervlakken te construeren. Twee mogelijke manieren om de PES te construeren zijn gebruikt: De Grow-methode en de currugatie verminderingprocedure (CRP). De H_2 -dissociatiewaarschijnlijkheden zijn berekend aan de hand van de pure klassieke baanmethode (CT methode), de quasi-klassieke baanmethode (QCT methode) en een quantumdynamica methode die gebruik maakt van een tijds-afhankelijk

golfpakket (TDWP). De H_2 -dissociatiesnelheidsconstanten zijn verkregen door middel van overgangstoestandtheorie (TST). Met gebruik van de QCT-resultaten, kunnen we de moleculaire bundel experimenten nabootsen met behulp van de curve van de H_2 -dissociatiewaarschijnlijkheid uitgezet tegen de “bundel-nozzle”-temperatuur.

In **Hoofdstuk 3** zullen we gebruik maken van DFT met de PW91 functionaal om Ti/Al(100) legering oppervlakken te modelleren en de dissociatie van H_2 op deze oppervlakken te beschrijven. Het doel van deze berekeningen is het begrijpen van de katalytische rol van titanium en de waterstofafgifte en -opname in $NaAlH_4$. Ti/Al oppervlakken zijn onderzocht met Ti-oppervlaktebedekkingen variërend van 1/4 tot 1 ML, met nadruk op $c(2 \times 2)$ structuren met oppervlakte-bedekkingen van een 1/2 tot 1 ML.

Bij een oppervlaktebedekking van een 1/2 ML heeft de energetisch meest gunstige $c(2 \times 2)$ structuur (Model-2), met de laagste energie van Ti per Ti atoom in Al, Ti atomen in de tweede laag. Bij 1 ML bedekking heeft de energetisch meest gunstige structuur (Model-3) Ti atomen in de eerste en derde laag. Dit model heeft wederom een $c(2 \times 2)$ structuur en de Ti atomen in de derde laag bevinden zich recht onder de titanium atomen in de eerste laag. In Model-2 verlaagt de aanwezigheid van Ti de barrière voor H_2 -dissociatie van 0.96 eV voor een puur Al(100) oppervlak (Model-1) naar 0.63 eV. In Model-3 verlaagt de aanwezigheid van Ti de barrière voor H_2 dissociatie zelfs nog verder, tot ongeveer 0.23 eV, hoewel de bindingsenergie van Ti is verhoogd met ongeveer 0.23 eV/Ti atoom vergeleken met Model-2. Modellen met 1 ML en 1/4 ML oppervlaktebedekkingen, waar Ti atomen zich alleen in de eerste laag bevinden, beschikken over nog lagere energie-barrières voor H_2 dissociatie, maar deze modellen hebben veel hogere bindingsenergieën for Ti in de Al(100) slabs en de Ti-Ti afstanden in deze structuren zijn niet in overeenstemming met de waarden gevonden in “Extended X-ray absorption fine structure” (EXAFS) experimenten. Aangezien de overeenkomst met het experiment uitstekend is voor de Ti-Ti afstand die is gevonden voor Model-3 en omdat Model-3 alleen een lage barrière heeft voor H_2 -dissociatie, kunnen we concluderen dat dit model waarschijnlijk het beste is voor de omschrijving van Ti-gekatalyseerde H_2 -dissociatie op Al(100) oppervlakken. De H_2 -dissociatie is exothermisch in Model-3 en er bevindt zich een moleculaire chemisorptie-put in het reactiepad met een diepte van 0.45 eV tussen de gasfase en de reactiebarrière.

Als het molecuul de chemisorptie-put benadert, komt het geen energie-barrière tegen. Dit kan worden uitgelegd door middel van een “two-center projected density of states” analyse. Dit laat zien dat er een gevulde-virtuele orbitaal attractie is tussen de H_2 σ_g en Ti $3d_{z^2}$ orbitalen. De barrière die de moleculaire chemisorptie-put en de gedissocieerde toestand scheidt, kan worden opgevat als het gevolg van de competitie tussen de toenemende overlap tussen de H_2 σ_u en Ti $3d_{xz}$ orbitalen en afnemende overlap tussen de H_2 σ_g en Ti $3d_{z^2}$ orbitalen. Dit suggereert dat, om H_2 -dissociatie te bevorderen, de hoeveelheid Ti die wordt toegevoegd hoog genoeg moet zijn om, in ieder geval voor een deel, een $c(2 \times 2)$ -Ti/Al(100) oppervlak te bewerkstelligen met een Ti-bedekking van 1

ML, waar Ti atomen aanwezig zijn in zowel de eerste als de derde laag van het oppervlak.

In **Hoofdstuk 4**, dat ook is gebaseerd op DFT, bestuderen we de elementaire reactie van H_2 -dissociatie op een met 1 ML Ti-bedekte Al(100) oppervlak. De Grow-methode wordt gebruikt om een 6D PES te maken van de elektronische grondtoestand met behulp van de BO- en statische oppervlak-benaderingen. H_2 -dissociatiewaarschijnlijkheden worden berekend met behulp van zowel de CT als de QCT methode en met behulp van de TDWP methode. De dynamisch interessante regio wordt gevonden in de buurt van het Ti atoom op het oppervlak, waar de moleculaire adsorptie-put zich in het laagste energiepad (MEP) bevindt. Dit leidt tot een hoge dichtheid van data punten in deze regio met de Grow-methode. De MEP is verbeterd in de Grow PES. De nieuwe H_2 -dissociatiebarrière is slechts 0.13 eV, dat is 0.10 eV lager dan de energiebarrière die wordt gerapporteerd in ons eerdere hoofdstuk.

We hebben de dissociatiewaarschijnlijkheden voor vier initiële quantumtoestanden van H_2 berekend met behulp van quasi-klassieke dynamica, *i.e.*: $(v = 0, j = 0)$, $(v = 0, j = 4, m_j = 0)$, $(v = 0, j = 4, m_j = 4)$ en de vibrationeel aangeslagen toestand $(v = 1, j = 0)$. De dissociatietrajecten voor lage botsingsenergieën (*i.e.*, onder 0.20 eV) van de rovibrationele grondtoestand en de rotationeel aangeslagen toestanden bevatten een relatief groot aantal terugkaatsingen van het oppervlak (tussen de 3–5), wat aangeeft dat in deze banen H_2 eerst “gevangen” wordt, voordat het dissocieert. In tegenstelling hiermee, dissocieert de vibrationeel aangeslagen toestand meer direct. Zowel rotationele als vibrationele excitatie bevordert de directe H_2 -dissociatie efficiënt met een “efficacy” van ongeveer 1.

De aanwezigheid van een diepe adsorptie-put aan de voorkant van de energiebarrière leidt tot statistisch gedrag: de H_2 -dissociatiewaarschijnlijkheid hangt alleen maar af van de totale (interne plus translationele) energie, met als uitzondering dat de vibrationele “efficacy” iets hoger is dan 1.0 voor lage reactiewaarschijnlijkheden.

De reactie van H_2 in zijn rovibrationele grondtoestand $(v = 0, j = 0)$ wordt ook beschouwd met behulp van quantumdynamica. De berekeningen laten zien dat de QCT methode de reactie accurater beschrijft dan de CT methode, in overeenstemming met wat eerder is gevonden in de meeste studies van H_2 + metaal-oppervlak systemen.

In **Hoofdstuk 5** bestuderen we de elementaire reactie van H_2 -dissociatie op een 1/2 ML Ti-bedekte Al(100) oppervlak. Ten eerste passen we de CRP methode toe om een 6D PES te construeren van de elektronische grondtoestand met behulp van de BO- en statische oppervlak-benaderingen. De PW91 en RPBE functionalen worden gebruikt om de potentiaal waarden te verkrijgen voor de respectievelijke potentiële energie-oppervlakken. H_2 -dissociatiewaarschijnlijkheden worden berekend door middel van zowel de CT als de QCT methode en met behulp van de TDWP methode. Wij hebben ook een moleculaire bundel simulatie gedaan en wij hebben de H_2 -dissociatiesnelheidsconstanten berekend als functie van de temperatuur.

H_2 -dissociatie op de 1/2 ML Ti/Al(100) oppervlak heeft een activatiebarrière van

0.65 eV als H₂ dissocieert van een brug naar een top “site” met de PW91 functionaal en een activatiebarrière van 0.84 eV met de RPBE functionaal.

Met quasi-klassieke dynamica hebben we de dissociatiewaarschijnlijkheden berekend voor de volgende quantum toestanden: $v = 0, j = 0 - 10$ en $v = 1, j = 0 - 7$, voor zowel de PW91 als de RPBE functionalen. Het toevoegen van translationele energie is ongeveer 3.0 (1.6) maal effectiever in het bevorderen van de reactie dan het toevoegen van rotationele (vibrationele) energie.

De reactie van H₂ in zijn rovibrationele grondtoestand ($v = 0, j = 0$) en in zijn vibrationeel aangeslagen toestand ($v = 1, j = 0$) zijn ook bestudeerd door middel van quantumdynamica. De berekeningen tonen aan dat de QCT methode accurater is in het beschrijven van de reactie dan de CT methode. Dit is in overeenstemming met eerdere studies van H₂ op metaal-oppervlakken. De snelheidsconstanten verkregen door de QCT methode zijn groter dan de snelheidsconstanten gevonden door middel van TST.

Samenvattend, gebaseerd op het bewijs dat titanium een belangrijke rol speelt in het proces van waterstofopslag van NaAlH₄, hebben we in Hoofdstuk 5 de H₂- dissociatiewaarschijnlijkheid op een 1/2 ML Ti-bedekt Ti/AL(100) oppervlak theoretisch berekend. Wij hopen dat onze voorspellingen van de reactiewaarschijnlijkheidscurves kunnen worden bevestigd door middel van moleculaire bundel experimenten.

List of publications

1. *A Theoretical Study of H_2 Reacting on Ti/Al(100) Surfaces*, J. C. Chen, J. C. Juanes-Marcos, A. Al-Halabi, R. A. Olsen and G. J. Kroes, *J. Phys. Chem. C*, **113**, 11027 (2009).
2. *Six-dimensional quasi-classical and quantum dynamics of H_2 dissociation on the $c(2 \times 2)$ -Ti/Al(100) surface*, J. C. Chen, J. C. Juanes-Marcos, S. Woittequand, M. F. Somers, C. Díaz, R. A. Olsen, and G. J. Kroes, *J. Chem. Phys.*, **134**, 114708 (2011).
3. *Six-dimensional quasi-classical and quantum dynamics of H_2 dissociation on the 1/2 ML Ti-covered $c(2 \times 2)$ -Ti/Al(100) surface*, J. C. Chen, M. Ramos, C. Arasa, J. C. Juanes-Marcos, M. F. Somers, A. E. Martínez, C. Díaz, R. A. Olsen, and G. J. Kroes, *Phys. Chem. Chem. Phys.*, submitted.
4. *A multifaceted approach to the hydrogen storage problem*, A. Churchard, E. Banach, A. Borgschulte, R. Caputo, J. C. Chen, D. Clary, K. Fijalkowski, H. Geerlings, R. Genova, W. Grochala, T. Jaroń, J. C. Juanes-Marcos, G. J. Kroes, I. Ljubić, N. Naujoks, J. Nørskov, R. A. Olsen, F. Pendolino, A. Remhof, L. Románszki, A. Tekin, T. Vegge, M. Zäch and A. Züttel, *Phys. Chem. Chem. Phys.*, submitted.

Curriculum Vitae

I was born on November 14, 1977 (or October 04, 1977 on the lunar calendar) in Shangzhou, Shaanxi Province, China. I entered middle school in 1990 and high school in 1993. During that time, I started to become interested in electricity and magnetism. Between September 1996 and July 2000, I studied at the Hainan University for my B.Sc. degree in Chemistry. After the third year of my study, I worked at the college laboratory as a volunteer doing experiments on organic chemistry, using infrared spectroscopy and guided by Wen-Xia Yu. In the summer holiday of 1997, I also investigated the environmental impact of and the procedures used by a sulfuric acid factory, 50 km away from my hometown. In August 2000, I worked at the Physical Chemistry group of the Xinjiang Institute of Chemistry, at the Chinese Academy of Sciences (CAS) in Urumqi. There, a procedure to synthesize saccharose ester with a yield over 95 % for industrial scale was successfully settled. In June 2001, I started to work in the State Key Laboratory of Molecular Reaction Dynamics, at the Institute of Chemistry, CAS, in Beijing. The project was to design the cavities for a Reflective Time-of-Flight Mass Spectrometer. In September 2002, I started the one-year course study of my M.Sc. program on Physical Chemistry at the Graduate School of CAS, in Beijing. One year later, I entered the State Key Laboratory of Molecular Reaction Dynamics to continue my M.Sc. program. My Master thesis contained a density functional theory study of transition metal/germanium binary clusters.

In December 2006, I started my Ph.D. research work at the Theoretical Chemistry group of Leiden University. My promotors are Prof. Dr. Geert-Jan Kroes and Prof. Dr. Roar A. Olsen. My co-promotor is Dr. Juan Carlos Juanes-Marcos, I was also supervised by Dr. Ayman Al-Halabi. The motivation of my research was to determine the catalytic role of titanium in hydrogenation and dehydrogenation of NaAlH_4 , through Ti/Al(100) surface models. My research focused on the quasi-classical and quantum dynamics of H_2 dissociation on the 1/2 ML and 1 ML Ti/Al(100) surfaces. In 2009, I also worked as a teaching assistant for the B.Sc. students in the College Physics courses given by Dr. Bart Vrijdaghs.

During my Ph.D. program, I also got many opportunities to present my research in group seminars, schools, workshops and conferences. I attended and gave two talks at the

winter schools “Theoretical Chemistry and Spectroscopy”, in 2007 and 2008 in Belgium. Between 2007 to 2010, at the annual “Marie Curie Network: Hydrogen” meetings held in Amsterdam, Reykjavik, Warsaw and Noordwijkerhout, I gave four talks. In another annual conference of the “NWO-CW Studiegroep Theorie en Spectroscopie” held between 2007 and 2011, I contributed two posters in 2007 and 2008, and one talk in 2011. At the “3rd Symposium Hydrogen and Energy” in 2009 in Switzerland, I presented a talk. I attended the “Winter School of Hydrogen” organized by Shell in February 2008 in Amsterdam, the “Summer School on Materials for the Hydrogen Society” in June 2008 in Reykjavik, the “Workshop of Quantum Transition State Theory” organized by Hannes Jónsson at University of Iceland, the “CINF Summer School” in 2009 in Denmark, and the “Marie Curie Network: COSY” in May 2010 at the University of Twente. I also attended the “Gordon Research Conference on Dynamics at Surfaces” in August 2011 at Salve Regina University in Newport, RI, the United States. I was also a member of the local organizing committee of the conference “Nano- and Surface Science Approaches to the Production and Storage of Hydrogen” (the fourth “Marie Curie Network: Hydrogen” meeting) in November 2010, Noordwijkerhout, the Netherlands.

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In 2011, an important event in my life was that I finished my Ph.D. thesis at the Theoretical Chemistry group of Leiden University. For me, this is a milestone in my academic research career. Thus, I would like to express the great gratitude to the people who have greatly helped me with my thesis.

Dr. Ayman Al-Halabi has supervised me and has closely interacted with me. He guided me initially to build the DFT slab models when I started my Ph.D. project.

During my Ph.D. program, I learned how to build potential energy surfaces from Dr. Cristina Díaz by using the Grow method. I learned transition state theory from Dr. Carina Arasa. I learned how to apply the SPO-DVR code to my system from Dr. Mark F. Somers. I learned how to use the DFT code VASP from Dr. Alvaro Valdés de Luxán. Dr. Krishnamohan G. Prasanna helped me to use the Visualization ToolKit, and he also taught me how to analyze the vibrational modes along the reaction path. Dr. Ali Awad Marashdeh helped me to understand the background to my project at the initial stage of my Ph.D. program, and he provided me with slab models of NaAlH_4 . Dr. Irene Groot provided me with her H_2 molecular beam parameters for the simulations. I have learned to use the quantum dynamics code MCTDH from Dr. Sylvain Woittequand, for preliminary calculations on my H_2 -surface system. Prof. dr. Simon W. de Leeuw taught me the free energy calculations by Monte Carlo simulation. Thanks for many discussions are due to Dr. T. P. M. Goumans and Prof. dr. Marc C. van Hemert. Dr. Ernst Pijper and Dr. T. J. Frankcombe taught me how to use and write Python scripts. I also gratefully acknowledge Dr. Mark F. Somers and Prof. dr. Marc C. van Hemert for generous help with the computer facilities. Many thanks to Prof. dr. Ewine van Dishoeck for her lectures on Astrochemistry; it is a wonderful course combining astronomy and chemistry in the Universe. Thanks to Prof. dr. Johannes Neugebauer for his lectures on Modern Quantum Chemistry. Thanks to Dr. Zheng-Wang Qu and his wife Dr. Hui Zhu for their help when they were in Leiden. Thanks also to Jelle Boereboom for his help with the translation of the Dutch summary. I also thank these people with whom I have had numerous discussions and communications: Dr. Ilaria Pino, Dr. Luca Sementa, Dr. Alexander Atamas, Drs. Carolin König, Drs. Alisa Solovyeva, Drs. Arseny Kovyreshin, Mark Wijzenbroek, Drs. Matteo Bonfanti, Dr. Michele Pavanello, Dr. Phillip Thomas and our Secretary

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