Chapter 4

Six-dimensional quasi-classical and quantum dynamics for H$_2$ dissociation on the 1 monolayer covered c(2 × 2)-Ti/Al(100) surface

This chapter is based on:

Abstract

Based on a slab model of H$_2$ 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, H$_2$ 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 H$_2$ 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 H$_2$ 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 × 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 $\text{H}_2 + \text{Ti/Al}(100)$, 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 $\text{H}_2$ on metal surfaces [23], because $\text{H}_2$ 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 $\text{H}_2$ 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 $\text{H}_2$ 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 $\text{H}_2$–surface reaction dynamics possible. Six-dimensional quantum dynamics has been successfully implemented to address the dissociative chemisorption of $\text{H}_2$ 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 $\text{H}_2$ 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 $\text{H}_2$ 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 × 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 $r^H_c = 0.46$ Å, $r^{Al}_c = 0.84$ Å and $r^{Ti}_c = 1.16$ Å. 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 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, and more details of the slab structure can be found in Chapter 3.

![Figure 4.1](image)

Figure 4.1: (a) (2 × 2) surface unit cell of Ti/Al(100) with lattice constant $a = 4.04$ Å. 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 $\theta$, and the azimuthal angle $\phi$.

A three-layer Ti/Al(100) slab model is employed in this work to study the H$_2$ dis-
association dynamics (see Fig. 4.1). Using a \((2 \times 2)\) 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 \(\text{H}_2\) 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 \(\text{H}_2 + \text{Ti/Al}(100)\) 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 \(5.0 \times 10^{-2}\) eV.

To get accurate vibrational modes, another DFT package Vienna \textit{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 \(\text{H}_2 + \text{Ru}(0001), \text{H}_2 + \text{Cu}(111)\) [18], \(\text{N}_2\) 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 \( \text{N}_2 + \text{Ru}(0001) \) [67, 68], \( \text{H}_2 + \text{Pt}(111) \) [62], \( \text{H}_2 + \text{Pd}(111) \) [69], \( \text{H}_2 \) on CO-precovered 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 \( R_i \to 0 \) are transformed away to \( Q_i \to \infty \)) [61]. For a system with \( N \) atoms, the number of interatomic distances is given by \( N(N-1)/2 \). Thus, in the system of \( \text{H}_2 + \text{Ti/Al}(100) \), \( N = 5 \) atoms are required (two hydrogen and three frozen surface atoms) to represent the six \( \text{H}_2 \) 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 interatomic distances, \( Q = \{Q_1, Q_2, ..., Q_{N(N-1)/2}\} \). For any configuration of the system \( Q \), a vector of \( 3N - 6 \) independent coordinates, \( \xi(Q) \), can be defined in terms of the inverse interatomic distances, via a singular value decomposition [59, 61, 62]:

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

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

\[
T_i(Q) = V[Q(i)] + \sum_{k=1}^{3N-6} \left[ \xi_k - \xi_k(i) \right] \frac{\partial V}{\partial \xi_k} \bigg|_{Q=Q(i)} + \frac{1}{2} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} \left[ \xi_k - \xi_k(i) \right][\xi_j - \xi_j(i)] \frac{\partial^2 V}{\partial \xi_k \partial \xi_j} \bigg|_{Q=Q(i)}. \quad (4.2)
\]

The value of the potential energy at data point \( Q(i) \), \( V[Q(i)] \), and the gradients with respect to \( \xi \) 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 $Q$ as a weighted average of the Taylor expansion terms $T_i (i = 1, ..., N_{\text{data}})$ calculated from each of the $N_{\text{data}}$ data points presented in the PES data set and all symmetry equivalent points:

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

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 $H_2 + Ti/Al(100)$ 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 $w_{g \circ i}(Q)$ for a given configuration $Q$ depends on how close it is to another configuration $Q(i)$ in the configuration space, and is defined by

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

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

$$v_i(Q) = \frac{1}{\|Q - Q(i)\|^2_p},$$

where we take $2p > 3N - 3$ to ensure that data points $Q(i)$ far from the configuration $Q$ 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

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

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. Distort-
ing 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 frag-
ments, 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 \( N_{\text{traj}} \) 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 \( N_{\text{traj}} \) configurations,

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

in which \( m \) is over all points recorded in the classical trajectories, and \( v_m \) is the unnor-
malized weight function in Eq. 4.6 of the difference between the recorded geometry \( Q(k) \)
and the geometry of one of the \( N_{\text{traj}} \) points in the numerator term. The integer \( i \) runs
over the points in the data set of \( N_{\text{data}} \), in the denominator term. The value of \( h(k) \) is
large when \( Q(k) \) 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 intertaplation by the weighted Taylor expansions is
the most inaccurate, according to a weighted mean square deviation criterium,

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

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

If a number of data points that have significant weight \( w_i [Q(k)] \) lead to widely
differing values of \( T_i [Q(k)] \) and \( V[Q(k)] \), 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.
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 \((2 \times 2)\) unit cell, which contains 73 data points along three different reaction paths for \(\text{H}_2\) dissociation on the Ti/Al(100) surface. The three one-dimensional reaction paths correspond to \(\text{H}_2\) 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 \(\Delta t\) 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 \(\text{H}_2\) 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 \(\text{H}_2 + \text{Ti/Al}(100)\) reaction, a total number of \(N_{\text{data}} = 4315\) 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 \(\text{H}_2\) 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 \(\text{H}_2 + \text{Pd}(111)\) [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 \(\text{H}_2 + \text{Pd}(111)\) 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
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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.

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 $V_A = V_z + V_{vib} + V_{rot}$ and $V_B = V_z - V_{vib} - V_{rot}$ 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\textsubscript{2} that are sampled while adding data points to the PES data set using the Grow method at different kinetic energy $E_{\text{kin}}$ (eV). The vibrational state is given by $v$, the rotational quantum number by $j$ and the magnetic rotational quantum number by $m_j$.

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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\textsubscript{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 $|L| = \sqrt{j(j + 1)}$, and the orientation of the $L$ vector is selected randomly with the constraint of

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

where $\theta_L$ is the angle between $L$ and the $Z$ axis (which is perpendicular to the surface).

The CT and QCT simulations are implemented in an isosceles right triangle of the $(2 \times 2)$ 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
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conditions [see Fig. 4.1(a)] and using the symmetry. All the initial configurations correspond to H\textsubscript{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 \( E_{\text{kin}} \) 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\textsubscript{2} molecule is considered to be dissociated. Otherwise, the H\textsubscript{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\textsubscript{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\textsubscript{2}, are not considered yet, which is the reason that we also need to calculate the H\textsubscript{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\textsubscript{2} coordinates used are the hydrogen inter-molecular distance \( r \), its center of mass coordinates \((X, Y, Z)\), the polar angle of orientation \( \theta \), and the azimuthal angle \( \phi \). To arrive at a quantum mechanical solution, we use the TDWP method [73] to solve the time-dependent Schrödinger equation,

\[
\hat{H} \Psi = i \frac{\partial \Psi}{\partial t}. \tag{4.10}
\]

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

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

Here, \( M \) is the mass of H\textsubscript{2} molecule, and \( \mu \) 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 \( (2 \times 2) \) 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(\( \Delta t \)) is proportional to \( \Delta t^3 \).
in the SPO method and it is unconditionally stable [36], \textit{i.e.,} the maximum time step $\Delta t$ 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,

$$\Psi(X, Y, Z, r, \theta, \phi) = \Phi_{v j}(r) Y_{jm_j}(\theta, \phi) \frac{1}{\sqrt{A}} e^{i \mathbf{K}_0 \cdot \mathbf{R}} \int dk_z b(k_z) \frac{1}{2\pi} e^{ik_zZ}.$$  \hspace{1cm} (4.12)

Here, $\Phi_{v j}(r)$ 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 \( A \), in which $A$ is a normalization factor (the surface area of the surface unit cell), $\mathbf{K}_0$ is the initial parallel momentum and $\mathbf{R}$ 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,

$$b(k_z) = \frac{2e^2}{\pi} e^{-(k_{av}-k_z)^2\zeta^2+i(k_{av}-k_z)Z_0},$$  \hspace{1cm} (4.13)

in which $\zeta$ 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 $\mathbf{K}_0 = 0$. Two initial wave packets with H$_2$ in its rovibrational ground state are propagated to obtain results for two kinetic energy ranges, \textit{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,

$$P_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin}) = |S_{vjm_j \rightarrow v'j'm'_jnm}(E_{kin})|^2.$$  \hspace{1cm} (4.14)
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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\textsubscript{j} = 0). Both distance and time are in atomic unit (a.u.), and energies are in eV, unless indicated otherwise.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>50 – 350 meV</th>
<th>300 – 850 meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial wave packet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center Z\textsubscript{0}</td>
<td>9.15</td>
<td>9.15</td>
</tr>
<tr>
<td>v</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>j</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m\textsubscript{j}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Propagation time step</td>
<td>2.50</td>
<td>1.0</td>
</tr>
<tr>
<td>Total propagation time t</td>
<td>115 000</td>
<td>112 000</td>
</tr>
</tbody>
</table>

| 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\textsubscript{j} in rotational basis | 18 | 18          |

| Analysis                      |             |              |
| Z\textsubscript{∞}            | 7.05        | 7.05         |

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

\[
P_r(E_{\text{kin}}) = 1 - \sum_{v'j'm'n} P_{vjm\rightarrow v'j'm'n}(E_{\text{kin}}).
\]  

(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 \(\text{H}_2\) spends most of its time near the surface Ti atom (Ti top site). The \(\theta\) anisotropy [the difference between the maximum and minimum value of \(V(\theta)\) at fixed values of \(X, Y, Z, r\) and \(\phi\)] 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 \(\theta\) angle is close to 90°, due to the large anisotropy of the potential with respect to \(\theta\) (the \(\text{H}_2\) molecule prefers to dissociate when the molecule is parallel to the surface). In contrast, the data are almost homogeneously distributed over \(\phi\) which indicates that changing \(\phi\) has little influence on the molecule-surface interaction. The \(\phi\) 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 \(\phi\). 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 \(\text{H}_2\) dissociating above a top Ti atom. The inset configurations illustrate that the lowest barrier geometry for \(\text{H}_2\) dissociating along the MEP is tilted, while in the one dissociating above the Ti atom \(\text{H}_2\) always remains parallel to the surface.](image)

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
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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 $15^\circ$ 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) and 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 $\theta$ and $\phi$, 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
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Figure 4.5: (a) PES 2D cut at \((Z, r)\) along the MEP \((X, Y, \theta \text{ and } \phi \text{ are fully relaxed})\); (b) 2D cut at \((Z, r)\) with COM fixed above the top Ti, \(\theta = 90^\circ \text{ and } \phi = 0.0^\circ\); (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 \(\theta\) and \(\phi\).
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Figure 4.6: Quasi-classical reaction probability for the para-H\textsubscript{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 \textit{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\textsubscript{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 \((E_{kin} = 0.10 \text{ eV})\), \(N_{reb}\) is 4.66 for dissociating \((v = 0, j = 0)\) H\textsubscript{2}, the value decreasing to 1.37 at \(E_{kin} = 0.90 \text{ eV}\). This finding indicates that in the low energy trajectories dissociation is promoted by trapping. During this trapping, configuration of the H\textsubscript{2} molecule can be adjusted to a proper orientation to pass the barrier. However, for large incident energy \(\textit{i.e.}, E_{kin} = 0.90 \text{ eV}\), 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 \(E_{kin} = 0.10 \text{ eV}\) and \(E_{kin} = 0.90 \text{ eV}\) respectively. From the comparison of the \(N_{reb}\) values of \(v = 0\) and \(v = 1\),
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
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$_2$ + Pt(211) [37, 87], H$_2$ + Pd(111) [88] and H$_2$ + 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

\[
\begin{align*}
\Theta_r(P_r) &= \frac{E_{j=0}^{\text{kin}}(P_r) - E_{j=4}^{\text{kin}}(P_r)}{E_{\text{rot}}(j = 4) - E_{\text{rot}}(j = 0)}, \\
\Theta_v(P_r) &= \frac{E_{v=0}^{\text{kin}}(P_r) - E_{v=1}^{\text{kin}}(P_r)}{E_{\text{vib}}(v = 1) - E_{\text{vib}}(v = 0)}. \\
\end{align*}
\]

Here, $E_{\text{kin}}^{j}$ ($E_{\text{kin}}^{v}$) 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 $E_{\text{rot}}$ ($E_{\text{vib}}$) 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 $\text{H}_2$ 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 $\text{H}_2$ 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 $\text{H}_2 + \text{Ti/Al}(100)$ 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 $\text{CH}_4$ 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 $\text{H}_2$ dissociation probability

Quantum dynamical calculations on the $\text{H}_2 + \text{Ti/Al}(100)$ reaction have been carried out for normal incidence of $\text{H}_2$ in its ($v = 0$, $j = 0$, $m_j = 0$) state.

The converged quantum reaction probability for $\text{H}_2$ dissociation is plotted in Fig. 4.9. Corresponding quasi-classical and pure classical reaction probabilities (the latter one with $E_{\text{vib}} = 0$ 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 $\text{H}_2$ 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 $E_{\text{kin}}$ 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-/e-) 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 $(j' = 0, m' = 0, n' = 0, m' = 0)$. 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 $(j'=0, m_j'=0, n'=0, m'=0)$. 
4.4 Conclusions

In this chapter, based on the density functional theory, we studied the elementary reaction of \( \text{H}_2 \) 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. \( \text{H}_2 \) 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 \( \text{H}_2 \) 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 \( \text{H}_2 \), 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 \( \text{H}_2 \) 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 \( \text{H}_2 \) 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 \( \text{H}_2 \) 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 \( \text{H}_2 + \) 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 \( \text{H}_2 \) 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


