Six-dimensional quasiclassical and quantum dynamics of H$_2$ dissociation on the c(2 × 2)-Ti/Al(100) surface

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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 a 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 quasiclassical 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 dependent on the total (internal and 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. © 2011 American Institute of Physics. [doi:10.1063/1.3567397]

I. 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$_4$). In a previous study of H$_2$ reacting on Ti/Al(100) surfaces, it was found that the most realistic model promoting H$_2$ dissociation is a one 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 a 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 a 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), energy transfer to motion of H$_2$ parallel to the surface (corrugation mediated selective adsorption), energy transfer to phonons, and energy transfer to electron–hole pair excitations. In order to determine to what extent these processes may contribute to sticking of H$_2$ at the temperatures (50–150 °C) relevant to the 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, 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 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 gas phase. Reactions proceeding over deep potential energy wells can be treated statistically, if the intermediates are sufficiently long lived. 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.

Increasing interest in the role of rotational and vibrational energy in promoting the molecule–surface reactivity is driven by the development of new theoretical methods and experimental tools allowing a more detailed insight into the details of a reaction. One of the widely studied systems, H$_2$ (D$_2$) + Cu(111) (Refs. 12–18, and 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)\textsuperscript{19-21} to the Cu(111) surface, which indicates that there is a steric effect in the dynamics. Both experimental\textsuperscript{16,17} and theoretical\textsuperscript{19} studies show that this system has rotational and vibrational efficacies of 0.40 and 0.65, respectively. Thus, the statistical model\textsuperscript{22} with a randomization of the initial conditions cannot be applied to this direct reaction. One question addressed here is whether the same conclusion can be drawn for the late barrier system H\textsubscript{2} + 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\textsubscript{2} on metal surfaces,\textsuperscript{23} because H\textsubscript{2} has a low electron affinity and the net charge transfer is almost zero during the process of dissociation.\textsuperscript{2,23,24} Thus, we neglect the electron–hole pair excitation. Due to the mismatch between the mass of H\textsubscript{2} and the 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\textsubscript{2} dissociation, and we only consider the motion in the six degrees of freedom (DOFs) on the ground state potential energy surface (PES).

Theoretical progress in gas–surface reaction dynamics\textsuperscript{11,25-31} combined with super computer facilities\textsuperscript{32} make six-dimensional (6D) quantum dynamics calculations of H\textsubscript{2}–surface reaction dynamics possible. Six-dimensional quantum dynamics has been successfully implemented to address the dissociative chemisorption of H\textsubscript{2} on Pd(100) (Refs. 25 and 33), Pd(110) (Ref. 34), Rh(100) (Ref. 33), Cu(100) (Refs. 30 and 35), Cu(111) (Refs. 18, 19, 26, and 28), Pt(111) (Refs. 23 and 36), Pt(211) (Ref. 37), Pd(111) (Ref. 38), Ru(0001) (Ref. 39), NiAl(110) (Refs. 40), and on sulfur-precovered Pd(100) (Ref. 41) and CO-precovered Ru(0001) (Ref. 42).

Based on a slab model of one ML Ti covered Ti/Al(100) surface,\textsuperscript{2} a 6D PES has been built by the density functional theory (DFT) (Refs. 43 and 44). Both the quantum and quasiclassical dynamics are calculated on it. Our results show that the H\textsubscript{2} dissociation probabilities obtained from quantum dynamics and quasiclassical 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 quasiclassical one up to 30.0% at incident energies above 0.30 eV.

The layout of this paper is as follows. The methodology and numerical details are presented in Sec. II, in which Sec. II A describes electronic structure calculations by DFT, Sec. II B describes the building of the 6D PES, Sec. II C describes the classical trajectory (CT) and quasiclassical trajectory (QCT) calculations, and Sec. II D describes the time-dependent wave-packet (TDWP) calculations. Results are presented and discussed in Sec. III. Specifically, Sec. III A shows the location of the data points and cuts through the PES. Section III B focuses on the H\textsubscript{2} dissociation probability calculated by QCT. In Sec. II C, comparisons of the CT, QCT, and TDWP results are presented. Finally, conclusions and an outlook are presented in Sec. IV.

II. METHODOLOGY AND NUMERICAL DETAILS

A. Electronic structure calculations and slab model

The DFT code DACapo (Ref. 45) is used to study H\textsubscript{2} dissociation on the one ML c(2 \times 2)-Ti/Al(100) slab model with Ti atoms in the first and third layers. The PW91 functional,\textsuperscript{46} which has been shown to give reasonably good results for H\textsubscript{2} dissociating on the NiAl(110) alloy surface,\textsuperscript{40,47} is employed to describe the exchange-correlation energy of the electrons. The ion cores are described by ultrasoft pseudopotentials,\textsuperscript{48} with core cutoff radii of $r^H_c = 0.46 \, \text{Å}$, $r^C_c = 0.84 \, \text{Å}$, and $r^{\text{Ti}}_c = 1.16 \, \text{Å}$. 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\textsuperscript{49} method, using a set of $6 \times 6 \times 1$ k-points. In the Z direction (perpendicular to the surface, see Fig. 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 $a = 4.04 \, \text{Å}$, and more details of the slab structure can be found in Ref. 2.

A three-layer Ti/Al(100) slab model is employed in this work to study the H\textsubscript{2} dissociation dynamics (see Fig. 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 H\textsubscript{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\textsuperscript{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 and 0.13 eV, respectively (converged values calculated with the four-layer slab model are 0.45 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\textsubscript{2} + Ti/Al(100) reaction (discussed in the next section, II B). 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\textsuperscript{-2} eV.

Our tests also show that the PW91 functional gives results similar to the Perdew-Burke-Ernzerhof (PBE) functional,\textsuperscript{50} which is expected because the PBE functional was designed to reproduce PW91 energies.\textsuperscript{50} We also tested the revised Perdew-Burke-Ernzerhof (RPBE) functional\textsuperscript{51} and found that it typically gives higher barriers than the PW91 functional, by about 0.25 eV. This is in accordance with recent theoretical\textsuperscript{50} and experimental\textsuperscript{52} works on H\textsubscript{2} + Ru(0001), H\textsubscript{2} + Cu(111) (Ref. 18), $N_2$ on W(100), and W(110) surfaces,\textsuperscript{53} 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.\textsuperscript{18}
B. Modified Shepard (MS) interpolation method and “growing” of the six-dimensional PES

To obtain a global PES, we have used a MS interpolation procedure\textsuperscript{54–57} initially developed by Collins and co-workers for gas phase reactions, and later adapted for studying the molecule–surface dissociative chemisorption reaction.\textsuperscript{58} The procedure of the application of the MS interpolation is informally known as the “Grow” method,\textsuperscript{54–57} in which the energies 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 quasiclassical trajectories. The MS interpolation method is efficient and accurate\textsuperscript{59,60} compared with the corrugation reducing procedure developed by Busnengo and co-workers.\textsuperscript{61,62}

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\textsubscript{2} on Ru(0001) (Refs. 63 and 64), H\textsubscript{2} + Pt(111) (Ref. 58), H\textsubscript{2} + Pd(111) (Ref. 65), H\textsubscript{2} on CO-precovered Ru(0001) (Ref. 42), and CH\textsubscript{4} + Ni(111) systems (Refs. 66 and 67).

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.\textsuperscript{57} For a system with \( N \) atoms, the number of interatomic distances is given by \( N(N − 1)/2 \). Thus, in the system of H\textsubscript{2} + Ti/Al(100), \( N = 5 \) atoms are required (two hydrogen and three frozen surface atoms) to represent the six H\textsubscript{2} DOFs, using two Ti atoms and one Al atom that form an isosceles right triangle.

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

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

(1)

The value of the potential energy at the data point \( \mathbf{Q}(i) \), \( V[\mathbf{Q}(i)] \), 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 \( \mathbf{Q} \) as a weighted average of the Taylor expansion terms \( T_i(\mathbf{Q}) \), \( V[\mathbf{Q}(i)] \), 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.

In Eq. (2), \( G \) 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\textsubscript{2} + Ti/Al(100) system [see the isosceles right triangle with two Ti atoms and one Al atom mentioned above in Fig. 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. (1), also see Fig. 1.

An advantage of the MS interpolation method is that the sampling of data points can be performed nonuniformly 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, 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. In the variance criterium, 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.

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 H2 dissociation on the Ti/Al(100) surface. The three one-dimensional reaction paths correspond to H2 dissociation on top Ti, top Al, and hollow sites.

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 the 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 has been added to the PES, the reaction probability for a number of initial H2 rovibrational states and collision energies is computed by running 5000 quasiclassical 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 H2 + 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 H2 initial states with several incident energies is shown in Fig. 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 the Monte Carlo sampling have small absolute errors in them. In the non-activated system H2 + Pd(111) studied by Busnengo and co-workers, it was found that low energy trajectories can also explore large parts of the PES. In their system, 83% of the trajectory configurations were added in the exit channel even at a low incident energy of 25 meV, and in this aspect the H2 + Pd(111) system differs from the activated system studied here.

C. CT and QCT calculations

As already mentioned, quasiclassical trajectories were run to find and sample the dynamically relevant regions of the PES during the Grow process, and to compute reaction probabilities. The initial rovibrational energy of the H2 molecule is taken into account by sampling the initial condition of the trajectories from a microcanonical ensemble. The velocities of H-atom 1 and 2 are calculated using

\[ v_1 = v_{\text{kin}} + v_{\text{vib}} + v_{\text{rot}} \]

and

\[ v_2 = v_{\text{kin}} - v_{\text{vib}} - v_{\text{rot}}, \]

respectively, in which $v_{\text{kin}}$ is the velocity in the Z direction calculated as $\sqrt{2E_{\text{kin}}/M}$, where $E_{\text{kin}}$ is the incidence energy and $M$ is the mass of H2, $v_{\text{vib}}$ ($v_{\text{rot}}$) 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 the helicopter rotationally excited state ($v = 0$, $j = 4$, $m_j = 4$), the initial energy of the trajectories also includes the rotational energy $E_{\text{rot}} = 0.14$ eV. For the first vibrationally excited state ($v = 1$, $j = 0$) the vibrational energy is set to $E_{\text{vib}} = 0.78$ eV. Normal incidence is modeled 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 potential.\(^6^8\) 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 \(\text{H}_2\)–surface reactions than the purely classical method.\(^1^1,^3^1\)

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. 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. 1(a)] and using the symmetry. All the initial configurations correspond to \(\text{H}_2\) in the gas phase, with \(Z = 4.0\) Å above the surface unit cell, see Fig. 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 I. If the final H–H distance is larger than 2.64 Å, the \(\text{H}_2\) molecule is considered to be dissociated. Otherwise, the \(\text{H}_2\) 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 \(\text{H}_2\) has a velocity pointing toward the vacuum. The reaction probability in the microcanonical 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 which should be important for \(\text{H}_2\) are not considered yet, which is the reason that we also need to calculate the \(\text{H}_2\) dissociation probabilities by the quantum wave packet method in Subsection II D 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.

### D. TDWP calculations

In the quantum dynamics, the six \(\text{H}_2\) coordinates used are the hydrogen intermolecular 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\(^6^9\) to solve the time-dependent Schrödinger equation,

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

The 6D Hamiltonian operator including the translational, vibrational, rotational, and potential energy terms is given by\(^1^1\)

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

Here, \(M\) is the mass of the \(\text{H}_2\) molecule, and \(\mu\) is the reduced mass associated with the vibrational motion. \(V_{6D}\) is the 6D Grow potential discussed in Sec. II B, 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 paper, a pseudospectral method is used to propagate the wave packet, in which the Hamiltonian is symmetrically decomposed as a noncommutative form by using the split-operator (SPO) method.\(^7^0\) The error per time step (\(\Delta t\)) is proportional to \(\Delta t^3\) in the SPO method and it is unconditionally stable,\(^3^6\) 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.\(^1^1,^3^6,^7^0\)

In our implementation,\(^3^6\) the initial wave packet is given by the formula,

\[
\Psi(X, Y, Z, r, \theta, \phi) = \Phi_{\nu j}(r)Y_{jm_j}(\theta, \phi) \frac{1}{\sqrt{A}} \epsilon^{i\vec{K} \cdot \vec{r}} \times \int dk_z b(k_z) \frac{1}{2\pi} \epsilon^{ik_z Z}.
\]

Here, \(\Phi_{\nu j}(r)\) and \(Y_{jm_j}(\theta, \phi)\) are the \(\text{H}_2\) vibrational and rotational eigenfunction, respectively, and \(\nu, j, m_j\) are the corresponding rovibrational quantum numbers. The initial parallel motion of the wave packet along \(X\) and \(Y\) is described by \((1/\sqrt{A})\epsilon^{i\vec{K} \cdot \vec{r}}\), in which \(A\) is a normalization factor (the...
surface area of the unit cell), \( \mathbf{K}_0 \) is the initial parallel momentum, and \( \mathbf{R} \) is 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

\[
b(k_z) = \frac{2\xi^2}{\pi} e^{-\frac{1}{4}(k_{av} - k_z)^2} e^{i(k_{av} - k_z)Z_0},
\]

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

In this paper, only normal incidence is considered and thus \( \mathbf{K}_0 = 0 \). Two initial wave packets with \( \mathcal{H}_2 \) in its rovibrational ground state are propagated to obtain results for two kinetic energy ranges, i.e., 50–350 and 300–850 meV. More computational details are listed in Table II, and the method used is described fully in Ref. 36. The converged grid spacings for \( Z \) and \( r \) are found to be 0.15 and 0.085 a.u. in the high energy range, respectively, see Table II.

The discrete potential energy values and the wave packet are defined on the same grid. The wave function on \( X, Y, Z, \) and \( r \) represented by the discrete variable representation (DVR), effectively using a plane-wave basis-set.\(^{71,72} \)

The angular momentum part of the wave function is represented by a finite basis representation (FBR), using orthonormalized associated Legendre polynomials as basis functions. Gauss–Legendre and Fourier transformations are used to transform the wave function from the FBR to the DVR.\(^{73,74} \) Quadratic form optical potentials\(^{75} \) 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,\(^{76–79} \) in which the scattered wave packet is projected at \( Z = Z_\infty \) onto the free particle states. The scattering probability at an incident energy \( E_{\text{kin}} \) for a transition from the initial state to the final state can be obtained from the S-matrix by

\[
P_{r(E_{\text{kin}})} = 1 - \sum_{v'j'm'n} P_{v'j'm'n}(E_{\text{kin}}). \tag{9}
\]

### III. RESULTS AND DISCUSSION

#### A. PES obtained from the “Grow” method

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. 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. 3(a)]. Another projection of the data points on \((X, Y)\) [Fig. 3(b)] shows that \( \mathcal{H}_2 \) 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. 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 \( \mathcal{H}_2 \) 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 a higher precision of the potential.

Using the procedure introduced in Sec. II B, the 6D PES was obtained by MS interpolation. The one-dimensional potential along the MEP obtained from Grow is shown in Fig. 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) (Ref. 80) 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

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**Table II.** 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.

<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_0 )</td>
<td>9.15</td>
<td>9.15</td>
</tr>
<tr>
<td>( v )</td>
<td>0</td>
<td>0</td>
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the COM of H₂ was fixed above the top Ti site and kept parallel to the surface during dissociation. However, for the lower barrier from the Grow potential, H₂ 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.\textsuperscript{[81]} using climbing images nudged elastic band\textsuperscript{[82]} calculations. When the COM of H₂ is restricted to be above the top Ti site,\textsuperscript{[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. 5. 2D elbow plots for H₂ dissociating along the MEP and the top Ti site are shown in Figs. 5(a) and 5(b), respectively. The 2D cut along the MEP corresponds to the one-dimensional plot in Fig. 4 with a well depth of 0.43 eV and a barrier height 0.13 eV. Figures 5(c) and 5(d), show that the barrier for H₂ dissociation is much higher above the Al top site and the hollow site, respectively. In Figs. 5(e) and 5(f) 2D cuts along \((X, Y)\) are shown, fixing \( r \) at the bond length of the molecular adsorption well value and the barrier position value while relaxing \( \theta \) and \( \phi \), respectively. In Fig. 5(f), four potential wells (at 0.55 a.u. away from the middle of

FIG. 4. Energies along the MEP as obtained from the Grow potential as shown by the solid line, as well as the reaction path for H₂ dissociating above a top Ti atom. The inset configurations illustrate that the lowest barrier geometry for H₂ dissociating along the MEP is tilted, while in the one dissociating above the Ti atom H₂ always remains parallel to the surface.

FIG. 5. (a) PES 2D cut at \((Z, r)\) along the MEP \((X, Y, \theta, \phi)\) are fully relaxed); (b) 2D cut at \((Z, r)\) with COM fixed above the top Ti, \( \theta = 90^\circ \) and \( \phi = 0^\circ \); (c) same as (b) fixed at top Al; (d) same as (b) fixed at hollow site. Figures (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 \( \phi \).
the unit cell) can be found around the Ti atom (in the middle of the unit cell), corresponding to the barrier positions of H₂ dissociation.

B. Quasiclassical H₂ dissociation probabilities

On the PES constructed from the MS interpolation method, 6D quasiclassical dynamical trajectory calculations are performed, in which the ZPE of the H₂ molecule is considered. Reaction probabilities are obtained for the following initial H₂ states (see Fig. 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 H₂ 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. 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 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 the 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. 7. A rebound occurs if the velocity of H₂ in the Z direction changes from negative to positive, thus \(N_{reb} > 1\) is an indication of trapping. In Fig. 7(a), a general trend observed is that \(N_{reb}\) decreases with the 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 \((v = 0, j = 0)\) H₂, 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 H₂ 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. 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 \(v = 1\), we see that \(v = 1\) H₂ 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 H₂ 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. 7(a)].

For the reflected trajectories in Fig. 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 \((v = 0, j = 0)\) H₂]. The comparison of the two panels in Fig. 7 is consistent with the conclusion that in the less trapped trajectories H₂ 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 H₂ molecule is the main mechanism leading to the dissociation for the rovibrational ground state \((v = 0, j = 0)\). Similar results were
previously obtained for the H$_2$ + Pt(211) (Refs. 37 and 83), H$_2$ + Pd(111) (Ref. 84), and H$_2$ + Pd(110) (Ref. 85) 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 $\Theta_v(P_v)$ (Refs. 86 and 87), may be calculated from

$$\Theta_r(P_r) = \frac{E_{r=j=0}^i(P_r) - E_{r=j=0}^{j=4}(P_r)}{E_{vib}(j=4) - E_{vib}(j=0)}$$

$$\Theta_v(P_v) = \frac{E_{vib}(j=1) - E_{vib}(j=0)}{E_{vib}(v=1) - E_{vib}(v=0)} \quad (10)$$

Here, $E_{kin}^i$ ($E_{kin}^{j=4}$) is the translational energy required to obtain a reaction probability $P_r$ when the H$_2$ molecule is initially in the rotational (vibrational) state $v$ ($j$), and $E_{vib}$ is the rotational (vibrational) energy of the H$_2$ molecule in the gas phase. An efficacy value of $\Theta_r(P_r)$ [$\Theta_v(P_v)$] 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. 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, $\Theta_v(P_v) = 1.20$ 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 the increasing dissociation probability. At a dissociation probability of 50.0%, the $\Theta_v(P_v)$ is around 1.0.

The reaction probability curves are replotted in Fig. 8 as a function of the total (internal and translational) energy. From this figure, it is seen that the H$_2$ dissociation probability mainly depends on the total energy and less on how the energy is divided between translation, rotation, and vibration.

The fact that the H$_2$ + 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 dependent on the energy. This agrees with the microcanonical unimolecular rate theory of dissociative chemisorption for CH$_4$ on Ni(100) developed by Harrison and co-workers, suggesting that it should be possible to compute accurate reaction rates with this theory.

C. Quantum dynamics of H$_2$ dissociation probability

Quantum dynamical calculations on the H$_2$ + 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. 9. Corresponding quasiclassical 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 calculations agree well with the quasiclassical ones in the low energy interval 50–200 meV, but the quantum dissociation probability are higher than the quasiclassical results by up to 0.06 (corresponding to a relative difference of 30.0%) for incident energies larger than 200 meV. The difference between quasiclassical and quantum reaction probabilities presumably tells us that the randomization of the energy in a quasiclassical trajectory may hinder the H$_2$ dissociation, especially at high incident energies. Classical dynamics results (see Fig. 9) show a reaction probability that is zero when $E_{kin}$ is below 0.20 eV.

To develop the development of the wave function in time, the projected probability density on the 2D $(Z, r)$ grid is shown in Fig. 10. In the high energy range (Figs. 10(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. 10(d)] and this node remains during the process of propagation. At $t = 6000$ a.u.,

FIG. 8. Reaction probability computed with quasiclassical dynamics but plotted as a function of the total (internal and translational) energy.

FIG. 9. Quantum reaction probability for H$_2$ initially in its ground rovibrational state $(v = 0, j = 0, m_j = 0)$. The quasiclassical and the classical results are also plotted.
only the $\nu' = 1$ 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, $P(v = 0, j = 0 \rightarrow \nu' = 1)$ is only 6.0%, the results suggest that trapping in the molecular adsorption well can arise from the vibrational excitation of $\text{H}_2$.

IV. CONCLUSIONS

In this paper, based on the density functional theory, we studied the elementary reaction of $\text{H}_2$ dissociation on a one ML Ti covered Al(100) surface. First, the Grow method is applied to build a 6D electronic ground state PES using the BO and static surface approximations. $\text{H}_2$ dissociation...
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