Transferability of the Specific Reaction Parameter Density Functional for H₂ + Pt(111) to H₂ + Pt(211)

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Supporting Information

Abstract: The accurate description of heterogeneously catalyzed reactions may require chemically accurate evaluation of barriers for reactions of molecules at the edges of metal nanoparticles. It was recently shown that a semiempirical density functional describing the interaction of a molecule dissociating on a flat metal surface (CHD₁ + Pt(111)) is transferable to the same molecule reacting on a stepped surface of the same metal (Pt(211)). However, validation of the method for additional systems is desirable. To address the question whether the specific reaction parameter (SRP) functional that describes H₂ + Pt(111) with chemical accuracy is also capable of accurately describing H₂ + Pt(211), we have performed molecular beam simulations with the quasi-classical trajectory (QCT) method, using the SRP functional developed for H₂ + Pt(111). Our calculations used the Born–Oppenheimer static surface model. The accuracy of the QCT method was assessed by comparison with quantum dynamics results for reaction of the ro-vibrational ground state of H₂. The theoretical results for sticking of H₂ and D₂ on Pt(211) are in quite good agreement with the experiment, but uncertainties remain because of a lack of accuracy of the QCT simulations at low incidence energies and possible inaccuracies in the reported experimental incidence energies at high energies. We also investigated the nonadiabatic effect of electron–hole pair excitation on the reactivity using the molecular dynamics with the electron friction (MDEF) method, employing the local density friction approximation (LDFA). Only small effects of electron–hole pair excitation on sticking are found.

1. Introduction

The heterogeneous catalysis community is highly interested in stepped surfaces because structure-sensitive catalyzed reactions often occur at edges of nanoparticles. These edges contain low-coordinated surface atoms, which resemble the atoms present at step edges of stepped surfaces. Consequently, a number of experiments have addressed dissociative chemisorption reactions at molecules on stepped surfaces, such as NO at steps on defective Ru(0001),1 H₂ on stepped Pt surfaces,2–8 N₂ at steps on defective Ru(0001),9,10 and methane on Pt surfaces,11,12 to name but a few examples. A much lower number of theoretical dynamics studies have addressed dissociative chemisorption on stepped surfaces, and these studies have looked at H₂ + Pt(211),13–17 H₂ + Cu(211),18,19 H₂ dissociation on defective Pd(111),20 and at CHD₃ + Pt(211).21

In view of the importance of dissociative chemisorption reactions on stepped surfaces to heterogeneous catalysis, it would obviously be useful to have a predictive procedure in place for accurately evaluating the interaction between a molecule and a stepped surface. Recent experimental work suggests that such a procedure may be based on experiments and dynamics calculations based on the semiempirical density functional theory (DFT) for the electronic structure, for the same molecule interacting with a low-index, flat surface of the same metal.12 As has now been established for several systems, dynamics calculations based on electronic structure calculations with the specific reaction parameter approach to DFT (SRP–DFT) are able to reproduce sticking measurements on such systems with chemical accuracy.12,25–28 Very recently, it has been shown that the SRP density functional (SRP-DF) for CHD₃ interacting with the flat Pt(111) surface is transferable to the same molecule interacting with the stepped Pt(211) system12 (transferability of the SRP DF from H₂ + Cu(111)12 to H₂ + Cu(100)),20 that is, among systems in which the same molecule interacts with different flat, low-index surfaces, had been established earlier.26 However, this finding just concerned only one specific system, and it is important to check whether this finding also holds for other systems. The main goal of this work is to investigate whether the SRP-DF recently determined for H₂ + Pt(111)28 is also capable of yielding chemically accurate results for H₂ + Pt(211).
The system of interest to our study (H\textsubscript{2} + Pt(211)) has first been studied theoretically. Olsen et al.\textsuperscript{13} computed a six-dimensional (6D) potential energy surface (PES) for the system with DFT, using the GGA functional due to Becke\textsuperscript{29} and Perdew\textsuperscript{30} (BP), and interpolating the DFT results with the corrugation reducing procedure (CRP).\textsuperscript{31} They next performed classical trajectory studies on this PES within the Born–Oppenheimer and static surface (BOSS) approximations. On the basis of these calculations, they were able to show that a trapping mechanism contributes a component to the sticking probability which is high at low incidence energy (\(E_i\)) and decreases monotonically with \(E_i\).\textsuperscript{14} In this mechanism, H\textsubscript{2} gets trapped at an unreactive site, that is, at the bottom of the step, and then diffuses to an atom at the top of the step edge, where it subsequently reacts.

Next, McCormack et al. also analyzed the other contributing mechanisms to the sticking of H\textsubscript{2} on Pt(211).\textsuperscript{14} Their classical trajectory calculations using the same PES as used before showed two additional mechanisms. A mechanism in which H\textsubscript{2} reacts directly at the step is nonactivated and contributes equally at all \(E_i\). In an additional mechanism, H\textsubscript{2} reacts on the terrace. In this mechanism, the reaction is activated, yielding a contribution to the sticking that rises monotonically with increasing \(E_i\). By scaling the contributions from the different mechanisms according to the different lengths of the (111) terraces in the Pt(211) and Pt(533) surfaces (both exhibiting (111) terraces and (100) steps), they\textsuperscript{14} were able to obtain good agreement with previous experiments on H\textsubscript{2} + Pt(533).\textsuperscript{6}

In two subsequent studies using the same PES, Luppi et al.\textsuperscript{15} investigated rotational effects with classical trajectory calculations, whereas Olsen et al.\textsuperscript{17} made a comparison between quantum dynamics (QD) and classical dynamics results for the reaction of (\(\nu = 0, j = 0\)) H\textsubscript{2}. According to the classical trajectory studies of Luppi et al., the trapping-mediated contribution to the reaction, which leads to a high sticking probability at low \(E_i\), but which contribution then quickly decreases with \(E_i\), should be present for low rotational states (\(j = 0\) and 1), but should disappear for states with intermediate \(j\). The reason they provided is that energy transfer to rotation should cause trapping for \(j = 0\) and \(j = 1\), whereas energy transfer from rotation should instead hinder trapping. Olsen et al.\textsuperscript{14} found that quasi-classical trajectory (QCT) calculations were in good agreement with QD results for high \(E_i\) (in excess of 0.1 eV). However, the QCT study overestimated the trapping-mediated contribution to the reaction at low \(E_i\), which was attributed to one mechanism operative for trapping in the classical calculations (excitation of the rotation) not being supported in QD, as the trapping well should not support rotationally excited bound states for their PES.\textsuperscript{17}

H\textsubscript{2} + Pt(211) has also been studied experimentally by Groot et al.\textsuperscript{7,8,32} Their molecular beam sticking probabilities were in reasonable agreement with the QD results for (\(\nu = 0, j = 0\)) H\textsubscript{2} of Olsen et al.,\textsuperscript{17} although the QD results based on the BP functional overestimated the sticking at high \(E_i\). Likewise, there were discrepancies at low \(E_i\) with the computed trapping-mediated contribution to the sticking being too low compared to the experimental result. In two subsequent papers, Groot et al. showed that the sticking on surfaces with longer (111) terraces and (100) steps (Pt(533) and Pt(755)) can successfully be modeled based on the contributing mechanisms to sticking at the step and at the terrace on Pt(211).\textsuperscript{6,32} Much like McCormack et al. had done before for Pt(533),\textsuperscript{14} they also used their results to analyze the contributions of facets and edges of Pt nanoparticles to H\textsubscript{2} dissociation proceeding on these nanoparticles.\textsuperscript{5}

The goal of the present paper is to test whether the SRP-DF for H\textsubscript{2} + Pt(111) is transferable to H\textsubscript{2} + Pt(211). For this reason, we will put emphasis on comparison of sticking probabilities computed with a PES obtained with the SRP-DF for H\textsubscript{2} + Pt(111) with the experimental results of ref 8, taking the experimental conditions (velocity distributions of the beams, nozzle temperatures \(T_n\) used) into account as fully as possible. Our calculations are done within the BOSS model and mainly use the QCT method for the dynamics. We will not reanalyze the mechanisms contributing to the reaction, simply noting that the dependence of the computed sticking probabilities on \(E_i\) is in accordance with conclusions arrived at earlier by Olsen et al.\textsuperscript{13} and McCormack et al.\textsuperscript{14} We find that overall, the computed sticking probability is in good agreement with the experiment for both H\textsubscript{2} and D\textsubscript{2} + Pt(211), suggesting that the transferability may well hold. However, at present, this conclusion is not yet certain because of uncertainties in the parameters needed to describe the molecular beams used in the experiments. Our results suggest that once more precisely defined experimental results become available, the comparison with the experiment should be revisited on the basis of QD calculations.

This paper is setup as follows. Section 2.1 describes the dynamical model, and Sections 2.2 and 2.3 describe the construction of the PES and the PES interpolation method. The dynamics methods used here are explained in Sections 2.4 and 2.5. Section 2.6 describes how we calculate the observables. Section 2.7 provides computational details. In Section 3, the results of the calculations are shown and discussed. Section 3.1 describes the computed PES. In Section 3.2, we compare the QCT results with the QD results. The isotope effect of the QCT results for reaction of (\(\nu = 0, j = 0\)) H\textsubscript{2} and D\textsubscript{2} is shown and discussed in Section 3.3. Section 3.4 provides theoretical results on molecular beam sticking probabilities and comparison with the experimental data. In Section 3.5, the effect of electron–hole pair excitation on the reactivity is discussed and the molecular dynamics with electron friction (MDEF) results are compared with the MD results for sticking. Conclusions are provided in Section 4.

2. THEORETICAL METHODOLOGY

2.1. Dynamical Model. The dynamics simulations presented in the following approach the true reaction dynamics of the system by assuming the reaction to take place on an ideal rigid Pt(211) surface at zero coverage. During the entire dynamics, the surface atoms are fixed at their initial equilibrium positions as obtained from DFT calculations. The dynamical degrees of freedom (DOF) treated here are the six DOF of H\textsubscript{2}. These are the center-of-mass (COM) position given by Cartesian coordinates \(X, Y, Z\) relative to a surface atom, the interatomic H–H distance \(r\), and the angular orientation of the molecule defined with respect to the macroscopic surface plane. As usual, \(X\) and \(Y\) are the lateral components of the COM position and \(Z\) is the molecule–surface distance. The orientation of the molecule is specified by the polar angle \(\theta \in [0, \pi]\) and the azimuthal angle \(\phi \in [0, 2\pi]\). The corresponding coordinate system is visualized in Figure 1.

2.2. Electronic Structure Calculations. In this work, electronic structure calculations are carried out using periodic DFT as implemented in the Vienna ab initio simulation
and Number of Layers in the Slab

\[ \alpha \]

of Lundquist and Langreth and co-workers. The latter value was set to 0.57 according to our previous work where we have determined this value to be suitable in order to bring the slab model. The resulting slab model obeys the symmetry of the \( p_\text{m} \text{h} \) plane group.

This is helpful in reducing the computational burden associated with the construction of the 6D PES, as we will show below. Similar to ref 18, the vacuum gap separating periodic slab images is about 16.2 Å. We use a \( \Gamma \)-centered \( 7 \times 7 \times 1 \) k-point mesh generated according to the Monkhorst grid scheme.

The energy cutoff, \( E_{\text{PAW}} \), used in the projector augmented wave (PAW) method was set to 450 eV. We employ Fermi smearing with a width of 0.1 eV. The optimal number of k-points and surface layers and the optimal \( E_{\text{PAW}} \) value were determined by convergence calculations, as summarized in Table 1. There we list the adsorption energy \( E_{\text{ads}} \) computed as difference between the minimum energy of \( \text{H}_2 \) at its equilibrium distance \( r_0 \approx 0.74 \text{ Å} \) in the gas phase (here about 6 Å away from the surface and parallel to the surface) and the dissociatively adsorbed \( \text{H}_2 \) on Pt(211), as depicted in Figure 1. \( E_{\text{ads}} \)-values are listed in Table 1 for different slab thicknesses, k-point meshes, and cutoff energies. The lattice constants of the rectangular \((1 \times 1)\) surface unit cell are \( L_X = 6.955 \text{ Å} \) and \( L_Y = 2.839 \text{ Å} \).

### 2.3. Representation of the PES

In order to construct a continuous electronic ground state PES for molecular hydrogen interacting with a rigid Pt(211) system, we adopt

![Figure 1. Coordinate systems for H₂ on Pt(211). (a) Top view of the \((1 \times 1)\) unit cell also showing the dissociated reference geometry of H₂ used to converge the computational setup with respect to the adsorption energy \( E_{\text{ads}} \). First and second layer Pt atoms are in silver and dark gray, respectively. H atoms are blue colored. (b) Side view of the slab model. The Z-axis (molecule−surface distance) in the standard coordinate system drawn in black is aligned with the normal to the macroscopic surface. X and Y are the lateral components of the COM position of H₂ indicated by a red dot. Furthermore, the angular orientation of H₂ is specified by the polar angle \( \theta \in [0, \pi] \) and the azimuthal angle \( \phi \in [0, 2\pi] \). (not shown). The angular orientation of H₂ in the internal coordinate system is defined with respect to the normal of the \((111)\) terrace, as shown in red. The two coordinate systems include an angle \( \chi \) of 20°. The corresponding angular coordinates are \( \theta', \phi' \). The surface lattice constants are \( L_X = 6.955 \text{ Å} \) and \( L_Y = 2.839 \text{ Å} \).](image)

Table 1. Adsorption Energies \( E_{\text{ads}} \) in eV for H₂ on Pt(211) Computed Using Different k-Point Meshes, Cutoff Energies \( E_{\text{PAW}} \) and Number of Layers in the Slab

| \( E_{\text{PAW}} \) [eV] | four-layer slab | five-layer slab |
|------------------------|----------------|----------------|
|                        | 350 | 400 | 450 | 500 | 350 | 400 | 450 | 500 |
| k-points               |     |     |     |     |     |     |     |     |
| \( 5 \times 5 \times 1 \) | 0.951 | 0.940 | 0.934 | 0.931 | 0.951 | 0.939 | 0.934 | 0.931 |
| \( 6 \times 6 \times 1 \) | 0.952 | 0.941 | 0.935 | 0.932 | 0.951 | 0.940 | 0.934 | 0.931 |
| \( 7 \times 7 \times 1 \) | 0.962 | 0.952 | 0.945* | 0.943 | 0.962 | 0.951 | 0.945 | 0.942 |
| \( 8 \times 8 \times 1 \) | 0.963 | 0.953 | 0.947 | 0.944 | 0.953 | 0.952 | 0.946 | 0.943 |

*The \( E_{\text{ads}} \)-value obtained with a converged computational setup is marked by an asterisk. The reference geometry of dissociated H₂ used to determine \( E_{\text{ads}} \) is shown in Figure 1.
the CRP\textsuperscript{31} which allows for a fast and accurate interpolation of DFT data points. The 6D PES accounts only for the six DOF of molecular hydrogen, as shown in Figure 1. Details about the CRP algorithm and its implementation in our in-house computer code are presented elsewhere.\textsuperscript{18} In the following, only a few principles of the CRP will be explained and a few details will be presented concerning the structure of the DFT data set. The interpolation of realistic globally defined PESs can become considerably error-prone when small geometrical alterations lead to strong changes of the system’s potential energy. Using the CRP, this problem can be avoided by first reducing large differences within the original DFT data points, $V^{\text{DFT}}$. The resulting reduced data set, $I^{\text{DFT}}(\vec{Q})$ is better suited for an interpolation which will yield the smooth function $I(\vec{Q})$ used to compute the final PES according to

$$V(X, Y, Z, r, \theta, \phi) = V(I(\vec{Q})) = V(I^{\text{DFT}}(\vec{Q})) + V^{\text{ref}}(\vec{Q})$$

(3)

Here, $\vec{Q} = (X_{i}, Y_{i}, Z_{i}, r_{i}, \theta_{i}, \phi_{i})^{T}$ is a discrete coordinate vector, labeled with the multidimensional index $i$, in the 6D space $Q = (X, Y, Z, r, \theta, \phi)^{T}$. For the reference function, $V^{\text{ref}}(\vec{Q})$, we are here using the sum of the two $H + Pt(211)$ interaction potentials which are also obtained via the CRP. They describe most of the repulsive features of the PES and are therefore particularly suitable for reducing the corrugation of the PES in the CRP as explained in refs.\textsuperscript{18,31}

In order to keep the number of DFT points to be computed as low as possible, we perform DFT calculations for specific angular orientations of $H_{2}$ labeled by $\{\theta, \phi\}$ in the following. They are defined in a modified coordinate system which is aligned with the vector normal to the (111) terrace and not with the vector normal to the macroscopic surface as is the case for the angular coordinates $\{\theta, \phi\}$. The corresponding transformations between the two coordinate systems were previously presented in ref \textsuperscript{42} and the Supporting Information of ref \textsuperscript{18}. In Tables 2 and 3, we list details about the DFT grid representation of the PES for the $H(D) + Pt(211)$ system as well as for the $H_{2}(D_{2}) + Pt(211)$ system (see also Figure 2). The latter is required to provide the reference PES $V^{\text{ref}}(\vec{Q})$ in eqs 2 and 3. Note that with the coordinate system chosen for the DFT calculations, for $H + Pt(111)$, a low minimum value of $Z$ is needed to map out the interaction of $H$ with $Pt(211)$ at the bottom of the step (see Table 2). In the CRP, this is required in order to remove the repulsive interaction in the $H_{2} + Pt(211)$ PES over the whole interpolation range before interpolation is carried out. Because of the (100) step, the surface roughness is increased and small molecule–surface distances need to be taken into account (here, $Z_{\text{min}} = -2.2\text{\ Å}$). Considering that we also describe molecular configurations in which $H_{2}$ stands perpendicular to the surface and that we represent large interatomic distances ($r_{\text{max}} = 2.5\text{\ Å}$), atomic repulsions must then also be represented for small atom–surface distances, down to $Z = -3.45\text{\ Å}$ (Figure 1).

![Figure 2](image-url)

Figure 2. Top view of a (1 $\times$ 1) unit cell of Pt(211). Indicated is the IW by a blue plane, and the blue dots represent the positions of $H$ and of the center of mass of $H_{2}$ at which DFT energy points were calculated in order to construct the 3D/6D PES. A few selected sites are labeled with top, brg (bridge), and t2b (top to bridge) and are further distinguished by numbers. Red dots indicate periodic images at the edge of the IW.

Table 2. Specification of the DFT Grid Used To Represent the Atomic Reference $H + Pt(211)$ Interaction Potential\textsuperscript{a}

| quantity | value | unit | remark |
|----------|-------|------|--------|
| grid range along $X$ on IW | [0, $L_{X}$] | Å | equidistant |
| grid range along $Y$ on IW | [0, $L_{Y}/2$] | Å | equidistant |
| grid range along $Z$ | $[-1.65, 7.05]$ | Å | |
| $N_{x}$ number of grid points in $X$ on IW | 18 | | |
| $N_{y}$ number of grid points in $Y$ on IW | 3 | | |
| $N_{z}$ number of grid points in $Z$ | 109 | | |
| $\Delta X$ grid spacing along $X$ | $L_{X}/18$ | Å | |
| $\Delta Y$ grid spacing along $Y$ | $L_{Y}/4$ | Å | |
| $\Delta Z$ grid spacing along $Z$ | 0.1 | Å | |
| representation of $V^{\text{ref}}$ reference potential | | | |
| grid range along $Z$ | [0, 7.05] | Å | |
| $N_{z}^{\text{ref}}$ number of grid points in $Z$ | 576 | | |

\textsuperscript{a}The grid along $Y$ is defined for the irreducible wedge (IW) which makes up only the half of the Pt(211) (1 $\times$ 1) unit cell (see Figure 2).
We apply the following interpolation order to generate a smooth function \( \mathcal{P}^{\text{DF}}(Q) \). First, we interpolate along the interatomic H–H distance \( r \) and the molecule–surface distance \( Z \) using a two-dimensional spline interpolation. Second, we interpolate along the polar angle \( \theta' \) using a trigonometric interpolation. Finally, we interpolate along the lateral positions \( X, Y \) and the azimuthal angle \( \phi' \) using a symmetry-adapted three-dimensional Fourier interpolation. The resulting PES is smooth, fast to evaluate and provides analytical forces.

### 2.4. MD Simulations

In this work, the dissociation dynamics of molecular hydrogen on Pt(211) is modeled using the QCT method, which is here obtained from a single DFT calculation. To compute the potential and forces as functions of the six molecular coordinates presented in Figure 1.

Following previous studies on the reactive scattering of diatomic molecules from metal surfaces, the effect of electron–hole pair excitation on the reaction of \( \text{H}_2(\text{D}_2) \) on Pt(211) can also be studied by scaling the LDFA–IAA friction coefficients. Here, we consider scaling factors of 1 (\( \eta = \eta^{\text{LDFA}} \)) and 2 (\( \eta = 2 \times \eta^{\text{LDFA}} \)). Here, we investigate what happens if the friction coefficients are multiplied by a factor of 2 because the LDFA–IAA friction model tend to come out larger. In the former case, we have performed calculations for \( T_s = T_{\text{el}} = 0 \) and 300 K, whereas in the latter case, only performed calculations at \( T_s = T_{\text{el}} = 0 \) K, that is, in the absence of random forces.

#### 2.5. QD Simulations

6D QD calculations are performed with the time-dependent wave packet method using our in-house wave packet propagation code by solving the time-dependent Schrödinger equation

\[
\frac{i\hbar}{\partial t} \Psi(\vec{Q}; t) = \hat{H} \Psi(\vec{Q}; t)
\]

Here, \( \Psi(\vec{Q}; t) \) is the corresponding nuclear wave function of molecular hydrogen at time \( t \). The Hamilton operator used in eq 6 accounts for the motion in the six molecular DOFs of \( \text{H}_2 \) and reads

\[
\hat{H} = -\frac{\hbar^2}{2M} \vec{\nabla}^2 - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \theta^2} + \frac{\hbar^2}{2\mu r^2} J^2(\theta, \phi) + V(\vec{Q})
\]

where \( \vec{\nabla} \) is the nabla operator, \( J(\theta, \phi) \) is the angular momentum operator for the hydrogen molecule, \( M \) is the molecular mass, and \( \mu \) is the reduced mass of \( \text{H}_2(\text{D}_2) \). The initial nuclear wave function is represented as a product of a wave function describing initial translational motion and a rotational eigenfunction \( \Phi_{i,j,m}(r, \theta, \phi) \) of gaseous \( \text{H}_2(\text{D}_2) \) characterized by the vibrational quantum number \( v_i \), the angular momentum quantum number \( j \), and the angular momentum projection quantum number \( m_r \). Therefore, the initial wave function reads

\[
\Psi(\vec{Q}; t_0) = \psi(\vec{k}_0, t_0) \Phi_{i,j,m}(r, \theta, \phi)
\]

where \( \vec{k}_0 = (k_0^x, k_0^y, k_0^z)^T \) is the initial wave vector. The wave function describing initial translational motion is given by

\[
\psi(\vec{k}_0, t_0) = e^{i(k_0^x x_0 k_0^y y_0 k_0^z z_0)} \int_{-\infty}^{\infty} \beta(k^2_z) e^{k_z^2/\sigma^2} \, dk_z
\]

Here, the initial wave packet \( \beta(k^2_z) \) is characterized by a half-width parameter \( \sigma \) according to

\[
\beta(k_0^2) = \left( \frac{2\sigma^2}{\pi} \right)^{-1/4} e^{-\sigma^2(\vec{k}-\vec{k}_0)^2} e^{-\frac{1}{4}(\vec{k}-\vec{k}_0)^2 Z_0}
\]

with \( \vec{K} \) being the average momentum and \( Z_0 \) is the position of the center of the initial wave packet.

The equations of motion were solved using the split-operator method. The motion in \( X, Y, Z \), and \( r \) was represented using Fourier grids. Quadratic optical potentials were used to absorb the wave function at the edges of the grid in \( r \) and \( Z \). A nondirect product finite basis representation was used to describe the rotational motion of \( \text{H}_2(\text{D}_2) \). To compute
reaction probabilities, first S-matrix elements were computed for dissociative and ro-vibrationally elastic and inelastic scattering, using the scattering matrix formalism of Balint-Kurti et al.\textsuperscript{61} These were used to compute probabilities for dissociative and ro-vibrationally elastic and inelastic scattering. The sum of these probabilities yields the reflection probability and subtracting from 1 then yields the reaction probability.

2.6. Computation of Observables. Using the quasi-classical method, we aim to model the sticking of H\textsubscript{2} (D\textsubscript{2}) on Pt(211) at conditions present in experiments we compare with by taking into account the different translational and ro-vibrational energy distributions characterizing the different molecular beams. At a nozzle temperature \( T_\text{n} \), the probability \( P_\text{beam} \) of finding molecular hydrogen in a specific ro-vibrational state \( \nu, j \) with a velocity \( v + dv \) in the beam is

\[
P_\text{beam}(\nu, j; T_\text{n}) dv = P_\text{int}(\nu, j; T_\text{n}) \times P_\text{vel}(\nu; T_\text{n}) dv
\]  
(11)

where the flux-weighted velocity distribution

\[
P_\text{vel}(\nu; T_\text{n}) dv = A v^3 \exp\left(-\frac{(v - v_0)^2}{\alpha^2}\right) dv
\]  
(12)

is normalized by a normalization constant \( A \) and characterized by a width parameter \( \alpha \) and the stream velocity \( v_0 \). The rotational state distribution is given by

\[
P_\text{int}(\nu, j; T_\text{n}) = \frac{\mathbb{w}(j) f(\nu, j; T_\text{n})}{\sum_{\nu', j'} \mathbb{w}(j') f(\nu', j'; T_\text{n})}
\]  
(13)

The weight \( \mathbb{w}(j) \) accounts for the different nuclear spin configurations of ortho- and para hydrogen molecules. For H\textsubscript{2}, \( \mathbb{w}(j) = 1/4 \) (3/4) for even (odd) \( j \)-values and for D\textsubscript{2}, \( \mathbb{w}(j) = 2/3 \) (1/3) for even (odd) values of \( j \). The function \( f(\nu, j; T_\text{n}) \) is defined as

\[
f(\nu, j; T_\text{n}) = (2j + 1) \exp\left(-\frac{(E_{\nu,j} - E_{\nu,j,0})/k_\text{B}T_\text{n}}{\text{vibrational energy distribution}}\right) \times \exp\left(-\frac{(E_{\nu,j} - E_{\nu,j,0})/0.8k_\text{B}T_\text{n}}{\text{rotational energy distribution}}\right)
\]  
(14)

The appearance of a factor of 0.8 in the rotational energy distribution reflects that rotational and nozzle temperatures assume the relation \( T_\text{rot} = 0.8T_\text{n} \) because of rotational cooling upon expansion of the gas in the nozzle.\textsuperscript{62} The experimental beam parameters for the H\textsubscript{2}/D\textsubscript{2} + Pt(211) systems are listed in Table 4.

The quasi-classical initial conditions are prepared using a Monte Carlo procedure described in ref \textsuperscript{44} and sample directly the probability distribution \( P_\text{beam} \). The resulting probability \( P_i \) for dissociative adsorption, scattering, and non-dissociative trapping of an ensemble of molecules is determined by the ratio

\[
P_i = \frac{N_i}{N}
\]  
(15)

where \( N_i \) stands for the number of adsorbed, dissociated, or trapped trajectories \( (N_{\text{ads}}, N_{\text{dist}}, N_{\text{trap}} \text{ respectively}) \) and \( N \) is the total number of trajectories computed for a specific energy point \( (E_i) \), where \( E_i \) denotes the average translational incidence energy of the molecule.

2.7. Computational Details. The time integration of eq 4 is done in Cartesian coordinates using a time step of \( \Delta t = 2.0\text{fs} \) with the stochastic Ermak–Buckholz propagator\textsuperscript{63} which also works accurately in the non-dissipative case. Further technical details are given in ref \textsuperscript{44,47} The maximal allowed propagation time for each trajectory is \( t_f = 10\text{ps} \). In the non-dissipative case, our QCT setup usually leads to an energy conservation error of smaller than 1 meV. All trajectories start at a molecule–surface distance of \( 7 \text{Å} \) and initially sample the ensemble properties of the experimental molecular beam, that is, we model the ro-vibrational state distribution according to the nozzle temperature as well as the translational energy distribution of the incidence beam. The parameters characterizing the molecular beam are given in Table 4, and details about their experimental determination are given in the Supporting Information. The initial conditions used in the quasi-classical simulations are determined using the Monte-Carlo algorithm explained in ref \textsuperscript{44}.

We compute \( N = 10000 \) trajectories per energy point and count trajectories as dissociatively adsorbed if they assume an interatomic H–H distance larger than 2.5 Å during the dynamics. Scattered trajectories are characterized by a sign change in the \( z \)-component of the total momentum vector and have to pass a molecule–surface distance of \( Z_{\text{inc}} = 7.1 \text{Å} \). We call a trajectory trapped if the total propagation time of 10 ps is reached and neither dissociation nor scattering has occurred.

The dissociative chemisorption of H\textsubscript{2} (\( \nu = 0, j = 0 \)) on Pt(211) is quantum mechanically investigated over a translational energy range of \( E_i \in [0.05, 0.75] \text{ eV} \) using two different wave packet propagations. The analysis line used to evaluate

| \( E_i \) [eV] | \( v_i \) [m/s] | \( \alpha \) [m/s] | \( T_\text{n} \) [K] | \( n \) in \( (E_i) = nk_\text{B}T_\text{n} \) | \( (E_{\text{inc}}) \) [eV] |
|---|---|---|---|---|---|
| H\textsubscript{2} | 0.004 | 626.5 | 55.9 | 293 | 0.048 | 0.116 |
| | 0.009 | 943.5 | 127.8 | 293 | 0.039 | 0.163 |
| | 0.013 | 1085.1 | 111.6 | 293 | 0.037 | 0.163 |
| | 0.014 | 1145.2 | 118.7 | 293 | 0.037 | 0.163 |
| | 0.025 | 1531.4 | 96.6 | 293 | 0.037 | 0.163 |
| | 0.035 | 1747.5 | 293.9 | 293 | 0.037 | 0.163 |
| | 0.043 | 2031.2 | 80.6 | 293 | 0.037 | 0.163 |
| | 0.132 | 3392.1 | 578.0 | 500 | 0.048 | 0.116 |
| | 0.181 | 3959.8 | 690.8 | 700 | 0.039 | 0.163 |
| | 0.169 | 4009.0 | 185.2 | 1300 | 0.039 | 0.163 |
| | 0.233 | 4442.8 | 862.5 | 900 | 0.048 | 0.116 |
| | 0.282 | 4838.8 | 1022.9 | 1100 | 0.039 | 0.163 |
| | 0.338 | 5223.2 | 1215.6 | 1300 | 0.039 | 0.163 |
| | 0.413 | 5617.0 | 1535.8 | 1500 | 0.039 | 0.163 |
| | 0.454 | 5790.7 | 1711.3 | 1700 | 0.039 | 0.163 |

The parameters were obtained from fitting the experimental TOF data to eq 6 in the Supporting Information. For pure H\textsubscript{2} and D\textsubscript{2} beams, we also provide \( n \) in \( (E_i) = nk_\text{B}T_\text{n} \) and the corrected average incidence energy \( (E_{\text{inc}}) = 2.7k_\text{B}T_\text{n} \).
the scattered fraction of the wave packet was put at \( Z_{\text{start}}^{\text{CAP}} = 6.6 \) Å. This is a suitable value because the PES is \( r \)-dependent only for all values \( Z \geq 6.6 \) Å, so it allows representing the wave function on a smaller grid using \( N_Z \) points in \( Z \) for all channels but the channel representing the initial state (called the specular state and represented on a larger grid called the specular grid, using \( N_Z^{\text{spec}} \) points). These parameters, and other parameters discussed below, are presented in Table 5.

### 3. RESULTS AND DISCUSSION

#### 3.1. Static DFT Calculations

Before we come to the dynamics calculations, we here first present general features of the interaction potential of atomic and molecular hydrogen and a Pt(211) surface. In Figure 3, we plot the minimum potential energy values for atomic H, assuming the optimal atom–surface distance \( Z_{\text{ads}} \) on a \((1 \times 1)\) supercell. The energies are given relative to the most stable configuration of H on Pt(211) which is here near to the brg1 position (see Figure 2). Because our DFT calculations do not include spin-polarization, the corresponding highest adsorption energy of 3.74 eV for a single H atom should to our experience be overestimated by \( \sim 0.7 \) eV. The contour line spacing is 0.03 eV.

![Figure 3. Minimum potential energy for H on Pt(211) for geometry-optimized atom–surface distances \( Z_{\text{ads}} \) on a \((1 \times 1)\) supercell. The energies are given relative to the most stable configuration of H on Pt(211) which is here near to the brg1 position (see Figure 2). The contour line spacing is 0.03 eV.](image)

The grids in \( Z \) start at \( Z = Z_{\text{start}} \) and share the same grid spacing. The grid in \( r \) is described in a similar way by the parameters \( r_{\text{start}}, N_r, \) and \( \Delta r \). The numbers of grid points used in \( X \) and \( Y \) \((N_X \) and \( N_Y)\) are also provided, as are the maximum value of \( j \) and \( m \) used in the basis set \((j_{\text{max}} \) and \( m_{\text{max}})\). The optical potentials used [also called complex absorbing potentials (CAPs)] are characterized by the value of the coordinate at which they start and end, and the value of the kinetic energy for which they should show optimal absorption.58,59 These values were taken differently for the regular and the specular grid in \( Z \). The time step \( \Delta t \) used in the split operator propagation and the total propagation time \( t_f \) are also provided. The initial wave packet is centered on \( Z_0 \) and is constructed in such a way that 95% of the norm of the initial wave function is associated with kinetic energies in motion toward the surface between \( E_{\text{min}} \) and \( E_{\text{max}} \) as also provided in Table 5.

#### Table 5. Characterization of the Two Different Wave Packet (WP) Calculations for \((\nu = 0, j = 0)\)H\(_2\) Incident Normally on Pt(211) for Translational Energies of \( E_j \in [0.05, 0.75] \) eV

| property | WP1 | WP2 | unit |
|----------|-----|-----|------|
| WP grid parameters | | | |
| range of X | \([0, L_X]\) | \([0, L_X]\) | \(a_0\) |
| \(N_X\) grid points in X | 36 | 36 | | |
| range of Y | \([0, L_Y]\) | \([0, L_Y]\) | \(a_0\) |
| \(N_Y\) grid points in Y | 12 | 12 | | |
| range of Z | \([-2.0, 19.45]\) | \([-2.0, 17.10]\) | \(a_0\) |
| \(N_Z\) | 144 | 192 | | |
| \(\Delta Z\) | 0.15 | 0.10 | \(a_0\) |
| \(N_Z^{\text{spec}}\) | 210 | 220 | | |
| range of r | \([0.80, 9.05]\) | \([0.80, 7.85]\) | \(a_0\) |
| \(\Delta r\) | 0.15 | 0.15 | \(a_0\) |
| \(j_{\text{max}} = m_{\text{max}}\) | 22 | 32 | | |
| CAPs | | | |
| \(Z^{\text{CAP}}\) range | \([12.55, 19.45]\) | \([12.50, 16.90]\) | \(a_0\) |
| \(Z^{\text{CAP}}\) optimum | 0.05 | 0.08 | eV |
| specular grid | | | |
| \(\rho^{\text{CAP}}\) start | 22.75 | 16.10 | \(a_0\) |
| \(\rho^{\text{CAP}}\) end | 29.35 | 19.90 | \(a_0\) |
| \(\rho^{\text{CAP}}\) optimum | 0.05 | 0.08 | eV |
| \(\rho^{\text{CAP}}\) range | \([4.10, 9.05]\) | \([4.55, 7.85]\) | \(a_0\) |
| \(\rho^{\text{CAP}}\) optimum | 0.05 | 0.20 | eV |
| propagation | | | |
| \(\Delta t\) | 2.00 | 2.00 | \(\hbar/\hbar_\text{s}\) |
| \(t_f\) | 3870.21 | 1741.60 | fs |
| initial wave packet | | | |
| energy range, \(E_j\) | \([0.05, 0.25]\) | \([0.20, 0.75]\) | eV |
| center of WP, \(Z_0\) | 16.45 | 14.30 | \(a_0\) |

*Specified are the grid parameters for the wave function and the PES, and parameters defining the complex absorbing potential in \( r \) and \( Z \), the center position \( Z_0 \) of the initial wave packet, and the corresponding translational energy range \( E_j \) covered.*

The grids in \( Z \) start at \( Z = Z_{\text{start}} \) and share the same grid spacing. The grid in \( r \) is described in a similar way by the parameters \( r_{\text{start}}, N_r, \) and \( \Delta r \). The numbers of grid points used in \( X \) and \( Y \) \((N_X \) and \( N_Y)\) are also provided, as are the maximum value of \( j \) and \( m \) used in the basis set \((j_{\text{max}} \) and \( m_{\text{max}})\). The optical potentials used [also called complex absorbing potentials (CAPs)] are characterized by the value of the coordinate at which they start and end, and the value of the kinetic energy for which they should show optimal absorption.58,59 These values were taken differently for the regular and the specular grid in \( Z \). The time step \( \Delta t \) used in the split operator propagation and the total propagation time \( t_f \) are also provided. The initial wave packet is centered on \( Z_0 \) and is constructed in such a way that 95% of the norm of the initial wave function is associated with kinetic energies in motion toward the surface between \( E_{\text{min}} \) and \( E_{\text{max}} \) as also provided in Table 5.
recognizes the typical elbow form of the PES along the vibration and translational energy plays in favor of reaction. Throughout the nine plots presented in Figure 4, one molecule do not only a adsorption state. They also in coordinates. On the one hand, the curvature of the minimum energy range of \( \frac{\theta}{90^\circ} \) coupling, which may facilitate dissociation in quasi-classical simulations artificially due to the zero-point energy conversion effect: the higher the curvature, the more coupling. This suggests that not only the dissociation of H\(_2\) on Pt(211) becomes strongly repulsive for very large values of \( \phi \). Interestingly, already small changes of the molecular geometry lead to significant changes of the topology of the PES. For example, moving H\(_2\) from the step edge to the bottom of the step while retaining its orientation, as shown in Figure 4c, yields a 2D-PES that has a large activation barrier of \( E^\dagger = 556 \text{ meV} \) and dissociation appears to be endothermic. Aligning now the molecular axis with the X-axis of the surface unit cell, as shown in Figure 4b, reduces somewhat the barrier but the PES becomes strongly repulsive for very large values of \( r \) \( (r > 2 \text{ Å}) \). This suggests that not only the dissociation of H\(_2\) on Pt(211) may be accompanied by a strong angular reorientation dynamics but also that associative desorption may set in after the molecule has experienced large interatomic stretches.

The different impact sites and initial orientations of the molecule do not only affect how large the barrier toward bond cleavage is and the length of the path toward a favorable adsorption state. They also influence the way in which vibrational and translational energy plays in favor of reaction. Throughout the nine plots presented in Figure 4, one recognizes the typical elbow form of the PES along the \( r \), \( Z \) coordinates. On the one hand, the curvature of the minimum energy paths in the elbows controls the vibration-translational \( (V-T) \) coupling, which may facilitate dissociation in quasi-classical simulations artificially due to the zero-point energy conversion effect: the higher the curvature, the more coupling.

On the other hand, the Polanyi rules\(^{67}\) relate the efficiency of translational and vibrational excitation of the incident molecule for reaction to the position of the barrier. In late-barrier system resembling the product state reaction is promoted vibrationally, whereas in early-barrier systems, reaction is more enhanced by translational excitation. For the H\(_2\) + Pt(211) system, vibrationally nonadiabatic \( V-T \) processes as well as the Polanyi rules are expected to come into play during the reaction dynamics. For example, we find relatively early barriers for impact situations shown in Figure 4b–d, suggesting a preference of translational excitation for reaction. Impact sites associated with a late barrier are shown in Figure 4f,h,i. In impacts on these sites, reaction is more likely to be promoted by initial vibrational excitation.

Reaction barrier energies and associated geometries for the nine incidence situations outlined in Figure 4 are specified in Table 6. Although the barriers to dissociation could be decreased somewhat when optimized with respect to \( \theta \) for cases in which H\(_2\) does not dissociate parallel to the step (Figure 4b,d,e,g,h), Figure 4 and Table 6 nevertheless provide a good view of the H\(_2\)–Pt(211) interaction. We find the latest \( (r = 1.62 \text{ Å}) \) and highest barrier \( (E^\dagger = 692 \text{ meV}) \) for molecules incident at the brg4 site (see also Figure 4h). This indicates a considerable range of activation energies (~700 meV) for the dissociation process. The \( Z^\dagger \)-values reported in Table 6 range from 0.51 Å at the top2 site (bottom of the step) to 2.79 Å at the top1 site (top of the step edge). This resembles to some extent the overall shape of the Pt(211) surface because step-top and step-bottom Pt atoms are displaced by \( \Delta Z = 1.27 \text{ Å} \).

The vdW-DF2 functional employed here yields not only rather large activation energies for the direct dissociation process but also considerable physisorption wells of ~72 meV located comparably far away from the surface. The presence of such wells may additionally contribute to the trapping dynamics of small molecules or may even increase the chance of redirecting the molecule toward non-dissociative pathways. Bärendt and co-workers\(^{13,14}\) previously reported on the importance of trapping as a mechanism for indirect dissociation of H\(_2\) on Pt(211). They used a PES that was constructed on the basis of standard GGA–DFT calculations, and the authors found only a shallow physisorption well for impacts at the bottom-step. When using the DF2-functional in the description of the dynamics of molecular hydrogen on Pt(211), as done in this work, the trapping mechanism may become more substantial, which may affect the computation of sticking probabilities for slow molecules.

### Table 6. Barrier Heights and Geometries for H\(_2\) on Pt(211) for the Geometries Shown in Figure 4\(^{a}\)

| Configuration | \( r^\dagger \) [Å] | \( Z^\dagger \) [Å] | \( E^\dagger \) [eV] |
|---------------|------------------|------------------|------------------|
| top1 (\( \phi = 90^\circ \)), Figure 4a | 0.75 | 2.79 | −0.083 |
| top2 (\( \phi = 0^\circ \)), Figure 4b | 0.90 | 0.59 | 0.396 |
| top2 (\( \phi = 90^\circ \)), Figure 4c | 0.88 | 0.51 | 0.556 |
| top3 (\( \phi = 90^\circ \)), Figure 4d | 1.00 | 0.99 | 0.118 |
| brg1 (\( \phi = 0^\circ \)), Figure 4e | 0.80 | 1.75 | 0.186 |
| brg3 (\( \phi = 0^\circ \)), Figure 4f | 0.94 | 0.73 | 0.639 |
| brg4 (\( \phi = 90^\circ \)), Figure 4g | 1.62 | 0.75 | 0.692 |
| brg5 (\( \phi = 120^\circ \)), Figure 4h | 0.89 | 1.37 | 0.318 |
| tzb1 (\( \phi = 90^\circ \)), Figure 4i | 1.34 | 1.53 | 0.035 |

\(^{a}\)Energies are given relative to the gas-phase minimum energy of H\(_2\).
3.2. Comparison of QCT and QD. Figure 5 shows the comparison between the QCT and QD results for $\text{H}_2$ ($\nu = 0$, $j = 0$). As already discussed in the introduction, the shape of the reaction probability curve in both the QD and the QCT dynamics arises from the presence of a trapping mechanism, which yields a contribution to the reactivity that decreases with incidence energy, and an activated mechanism, the contribution of which increases with incidence energy. As a result, the reaction of the $\text{H}_2$ molecule on Pt(211) exhibits a non-monotonic behavior as a function of the collision energy. The reaction probability curve shows very high dissociation probabilities at very low collision energies. The minimum value of the reaction probability is at an intermediate value of the collision energy, and the slope of the reaction probability curve becomes positive at higher collision energies.

As noted by McCormack et al.,14 with a GGA PES, nonactivated indirect dissociation may occur when a molecule hits the lower edge of the step on a nonreactive site, which showed the presence of a shallow chemisorption well on their PES. A difference with our PES is that physisorption can occur anywhere at the surface because of the presence of vdW wells for the PES computed with the vdW-DF2 correlation functional.

The QCT calculations reproduce the QD results at the higher incidence energies reasonably well. At low and intermediate energies, in the QD results, the trapping mechanism manifests itself by the occurrence of peaks in the reaction probabilities, with the peak energies corresponding to the energies of the associated metastable quantum resonance (trapped) states. The comparison suggests that at low and intermediate energies (up to 0.2 eV), the QCT results tend to overestimate the reactivity a bit. This could be due to two reasons. First, the increase of the reaction probability with decreasing energy at the lower incidence energy is understood to occur as a result of trapping of molecules entering the potential well, in which energy from the motion perpendicular to the surface is transferred into rotation and translational motion parallel to the surface.17 In the QD calculations, trapping should only be due to energy transfer to the motion parallel to the surface.17 However, classically, it is also allowed that energy is transferred from the motion toward the surface to the rotational DOFs.17 Second, the QCT calculations may suffer from an artificial effect called zero-point-energy leakage, that is, in QCT calculations, the quantization of vibrational energy may be lost and the original vibrational zero point energy may be transferred to other DOF.

3.3. Isotope Effects in QCT Results for Reaction of ($\nu = 0, j = 0$) $\text{H}_2$ and $\text{D}_2$. Comparison between the computed QCT reaction probability curves for $\text{H}_2$ and $\text{D}_2$ shows that the reaction probability of $\text{H}_2$ is higher than that of $\text{D}_2$ at the same incidence energy (see Figure 6). We attribute this to a zero-point energy effect. $\text{H}_2$ has more energy in zero point vibrational motion than $\text{D}_2$, so there is a higher probability that a given amount of this energy is transferred along the reaction coordinate. Gross and Schefler68 for $\text{H}_2$ dissociation on Pd(100) showed that in classical dynamics (no initial zero-point energy), there is no isotope effect between $\text{H}_2$ and $\text{D}_2$ in the sticking probabilities. At first sight, one might expect that steering is less effective for $\text{D}_2$ because of its higher mass and therefore less reaction for $\text{D}_2$ than $\text{H}_2$. On the other hand, $\text{D}_2$ is slower than $\text{H}_2$ at the same kinetic energy, so there is more time for the steering force to redirect the $\text{D}_2$ molecule to a nonactivated path. However, they found the quantum dynamical sticking probabilities of $\text{D}_2$ to be smaller than those of $\text{H}_2$. They suggested that this small difference should be a quantum dynamical effect and that the larger vibrational zero point energy of $\text{H}_2$ can more effectively be used to cross the reaction barrier.

No isotopic dependence and also no surface temperature dependence for the sticking probability were reported by the experimentalists,8 as shown in Figure 7 where we show the experimental sticking probability of $\text{H}_2$ (red symbols) and $\text{D}_2$ (black symbols) on Pt(211) as a function of average collision energy.
sticking probability as a function of average incidence energy. (In ref 8, the sticking probabilities were shown as a function of the incidence energy corresponding to the most probable energy for a density-weighted incidence energy distribution, see the Supporting Information).

3.4. Comparison of Molecular Beam Sticking Probabilities with Experiment. Parameters used for the molecular beam sticking simulations (previously extracted from experiments as discussed in the Supporting Information) of H₂ and D₂ on Pt(211) are given in Table 4.

The sticking probabilities extracted from molecular beam simulations for H₂ dissociation on Pt(211) are shown in Figure 8 with a comparison to the experimental results. In the figure, the red circles show the theoretical results obtained from simulating the experimental beam conditions. The black circles display the experimental results reported by Groot et al. (black symbols: experimental data from ref 8) are plotted beside the theoretical results (red symbols). The arrows and accompanying numbers show the collision energy difference between the interpolated theoretical results and experimental data.

![Figure 8](image-url)

**Figure 8.** Sticking probability for molecular beam of H₂ on Pt(211) simulated with QCT. For comparison, experimental results reported by Groot et al. (black symbols: experimental data from ref 8) are plotted beside the theoretical results (red symbols). The arrows and accompanying numbers show the collision energy difference between the interpolated theoretical results and experimental data.

The sticking probabilities extracted from molecular beam simulations for H₂ dissociation on Pt(211) are shown in Figure 8 with a comparison to the experimental results. In the figure, the red circles show the theoretical results obtained from simulating the experimental beam conditions. The black circles display the experimental results reported by Groot et al. (black symbols: experimental data from ref 8) are plotted beside the theoretical results (red symbols). The arrows and accompanying numbers show the collision energy difference between the interpolated theoretical results and experimental data.

the energy axis between experimental data points and the interpolated theoretical curve is [7−92] meV for H₂ + Pt(211) and [3−55] meV for D₂ + Pt(211). On this basis, our results for H₂ + Pt(211) do not yet agree with the experiment to be within chemical accuracy (≈43 meV). To find the mean deviation of the theoretically calculated sticking probability curve from the experimental results, we also calculated the mean absolute error (MAE) and mean signed error (MSE). We obtained a MAE of 40.8 meV and a MSE of 9.8 meV for H₂ and a MAE of 32.4 meV and a MSE of −0.4 meV for D₂. On this basis, the errors in the theoretical data in both cases are less than 1 kcal/mol ≈43 meV.

As already stated, the comparison between experimental and theoretical results is not yet good at the lower incidence energies. Two reasons might be involved, which are related to that being an important contribution to sticking from a trapping-mediated mechanism. The first reason concerns the inability of the QCT method to describe the sticking probability accurately when trapping contributes to reaction. The QCT results overestimate the contribution of trapping because of translation-to-rotation energy transfer, which is not allowed in QD descriptions (see Section 3.2). The QD calculations of Figure 5 suggest that for reaction of H₂ (ν = 0, j = 0), the reaction probability decreases faster with energy at low incidence energies if quantum effects are included, which goes in the right direction for getting better agreement with experiment. The other effect that could be important is surface temperature, which we do not include in our calculations. The initial reaction probability was experimentally determined at the surface temperature of 300 K. However, the experimentalists did not observe any surface temperature dependence. In our view, this makes it unlikely that the static surface approximation we used here is responsible for the discrepancy with experiment at low incidence energy.

Especially for H₂, our QCT results overestimate the experimental sticking probability at high average energies, as computed from the beam parameters available from fitting experimental TOF spectra (see the Supporting Information). One question we addressed is whether this could be due to errors arising from fitting these parameters, which is critically difficult especially at high incidence energies associated with short flight times. Now it is rather well known that for pure H₂ beams, the average translational energy should not exceed 2.7kBT∞ as no vibrational cooling occurs, and only about 20% rotational cooling. Comparing the average incidence energies of the pure H₂ beams in Table 4 with 2.7kBT∞ we however find that in most cases, the average incidence energies exceed 3kBT∞ and this also holds true for pure D₂ beams (see also Table 4). This suggests that the experimental average incidence energies extracted from the beam parameters were too high. By re-plotting the experimental results using average incidence energies Eav from equal to 2.7kBT∞ we can redo the comparison with the computed sticking probabilities, if we assume that the computed values do not much depend on the nozzle temperature through altered ro-vibrational state distributions. This is likely to hold true for nonactivated or weakly activated dissociation. As Figure 10 shows, this approach tremendously improves the agreement with experiment for the higher incidence energies at which the sticking is dominated by activated dissociation and for which the QCT results should be accurate (see Section 3.2): the agreement with experiment is now within chemical accuracy for these energies and pure H₂ beam conditions. For D₂, the agreement
is not as good as for H$_2$ for the lower incidence energies in the high-energy range (see Figure 11), which is perhaps due to the rotational cooling being somewhat more efficient for D$_2$ than for H$_2$, due to the lower rotational constant of D$_2$. This means that in Figure 11, the experimental data could move somewhat to the right (to higher energies), thereby improving the agreement with the experiment. Note also that in principle, the fits of the beam parameters are expected to be less error prone for H$_2$ than for D$_2$ because of longer flight times of D$_2$.

Another solution to the puzzle of why the average incidence energies calculated from the beam parameters did not correspond to $2.7k_B T_n$ for pure beams could be that the nozzle temperature was actually higher than measured. This could in principle be simulated by assuming that the nozzle temperature can be computed from the measured average incidence energy, instead of adapting the average incidence energy to the measured nozzle temperature. This was not pursued computationally, as it would only be expected to lead to a small increase of the computed sticking probability, and to somewhat larger discrepancies for H$_2$ + Pt(211), for which the agreement with experiment was worst to start with.

Above, we have suggested that the rotational cooling in a D$_2$ beam could be somewhat more efficient than that in the H$_2$ beam (due to the rotational constant of D$_2$ being lower). If this were true, this would suggest that we could have plotted the experimental data for the pure D$_2$ beams as a function of $(E_i) = c k_B T_n$ with $c$ somewhat larger than 2.7 (for instance, 2.75 or 2.8) in Figure 11. If this would be correct, this would increase the agreement between theory and experiment in this figure, as already discussed above. However, it should also alter the conclusion regarding the absence of an isotope effect drawn originally by the experimentalists: if this assumption would be correct, the sticking probabilities measured for H$_2$ should be somewhat higher than those for D$_2$, at least for the results from the pure H$_2$ and pure D$_2$ experiments. This would bring theory and experiment in agreement also regarding the qualitative conclusion on the isotope effect.

3.5. Comparison of MD and MDEF Results for Sticking. Figures 12 and 13 show the results of MD and MDEF calculations for H$_2$ + Pt(211) and D$_2$ + Pt(211). At low energies, adding electronic friction and doubling the friction coefficient increase the sticking probability for D$_2$. Doubling the electronic friction coefficient increases the sticking probabilities of H$_2$ only at intermediate energies. At higher incidence energies, adding electronic friction decreases the
sticking probability a little bit. Adding this energy dissipation channel reduces sticking somewhat at higher incidence energies because energy in the bond stretch coordinate is nonadiabatically dissipated to electron–hole pair excitation. Also, modeling the effect of the finite electronic temperature decreases the sticking probability at lower incidence energies, but there is no dramatic effect at higher incidence energies. The effect of $T_e$ is negligible for $(E_i) > 0.13 \text{ eV}$ and very small at lower incidence energy. At the lowest incidence energies, the electronic dissipative channel enhances the trapping and, therefore, the dissociation probability.\textsuperscript{72} The dissociation process is expected to increase in the presence of a trapping mechanism because once the molecule is trapped on the surface and starts to dissipate energy, it is difficult for the trapped molecule to recover the perpendicular translational energy to escape from the surface. The effect of including electron–hole pair excitations is therefore to increase the trapping-mediated contribution to the reactivity and thereby the reactivity. However, it keeps the direct mechanism almost unchanged. Raising the electronic temperature at lower incidence energies, that is, through the presence of hot electrons, leads to collisions of the hot electrons with the molecule that can excite the molecular DOFs and provide the trapped molecule with sufficiently high energy to get desorbed from the surface to the gas phase. Taking the electronic temperature in our calculations at lower incidence energies into account diminishes the trapping effect and therefore reduces the overall reactivity.

The good agreement between the MD and MDEF results at higher incidence energies confirms that the BOSS model, which does not consider electron–hole pair excitation, may accurately describe the dissociation of H$_2$ and D$_2$ on Pt(211) through the direct reaction mechanism at the terrace, and therefore, at higher incidence energies.

4. CONCLUSIONS

To address the question whether the SRP-DF functional derived for the H$_2$ + Pt(111) is transferable to the H$_2$ + Pt(211) system, we have performed calculations on the dissociation of H$_2$/D$_2$ on the stepped Pt(211) surface. We used the VASP software package to compute the raw DFT data. The CRP interpolation method was used to accurately fit these data and construct the 6D PES based on the PBEα–vdW-DF2 functional with $\alpha$ set to 0.57. The potential energy for H on Pt(211) for geometry optimized atom–surface distances on a $(1 \times 1)$ supercell was discussed and was compared with the previously developed PES of Olsen et al.\textsuperscript{42} We have also discussed features of the PES for H$_2$ dissociation on Pt(211) and reported on minimum barrier heights and associated geometries.

We have performed calculations within the BOSS model and within the MDEF model, in order to study nonadiabatic effects on the dissociation dynamics due to the creation of electron–hole pairs in the surface. The QCT method has been used to compute the initial-state resolved reaction probability and molecular beam sticking probability. The initial-state resolved reaction probability results obtained with the QCT method were compared with the results of QD calculations. The QCT calculations reproduced the QD results at the high-energy range but not at the low-energy range. The discrepancy between the results of these two dynamics methods at the low-energy regime was discussed. We have also shown and discussed the isotope effect in the QCT results of the reaction probability of $(\nu = 0, j = 0)$ of H$_2$ and D$_2$.

We have computed the sticking probabilities of molecular hydrogen and deuterium on Pt(211) and compared our theoretical results with the experimental data. Our theoretical results showed that the reactivity on Pt(211) is enhanced relative to Pt(111), in agreement with experiment. The lowest barrier height for reaction was found at the upper edge of the step. Reaction on the upper edge of the step is not activated. We have simulated molecular beam sticking probabilities and compared them with the experimental data of Groot et al.\textsuperscript{3} We have reported the energy shifts between the experimental data and the spline-interpolated theoretical data to be [7–92] meV for H$_2$ +Pt(211) and [3–55] meV for D$_2$ + Pt(211). Thus, chemical accuracy was not yet achieved in our theoretical results. However, it is well known that the average energy of pure H$_2$ beams should not exceed 2.7$k_B T_e$ because of the absence of vibrational cooling and the occurrence of only about 20% rotational cooling for a pure beam. Nevertheless, we found that in most cases, the average energies of the pure H$_2$ and the pure D$_2$ beams exceeded 3$k_B T_e$. Consequently, we have replotted the experimental results employing average energies equal to 2.7$k_B T_e$ and redone the comparison with computed sticking probabilities. With this modification, the agreement between experiment and theory tremendously improved for H$_2$. The agreement between theory and experiment for D$_2$ was not as satisfactory for H$_2$ at the lower incidence energies in the high-energy range. These results suggest that the experiments should be repeated and be reported for more accurately measured beam parameters to enable a better determination of the accuracy of the theoretical results.

Finally, we have presented the comparison of MD and MDEF results for the sticking probability for both H$_2$ and D$_2$ and discussed the effect of adding electronic friction and doubling the friction coefficient, and the effect of electronic temperature on the sticking at low and high incidence energies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b11018.

Details about the molecular beam parameters obtained from time-of-flight spectroscopy (PDF)

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REFERENCES

(1) Zambelli, T.; Wintterlin, J.; Trost, J.; Ertl, G. Identification of the “Active Sites” of a Surface-Catalyzed Reaction. Science 1996, 273, 1688–1690.
(2) Lu, K. E.; Rye, R. R. Flash desorption and equilibration of H₂ and D₂ on single crystal surfaces of platinum. Surf. Sci. 1974, 45, 677–695.
(3) Bernasek, S. L.; Somorjai, G. A. Molecular Beam Study of the Mechanism of Catalyzed Hydrogen-Deuterium Exchange on Platinum Single Crystal Surfaces. J. Chem. Phys. 1975, 62, 3149–3161.
(4) Christmann, K.; Ertl, G. Interaction of Hydrogen with Pt(111): The Role of Atomic Steps. Surf. Sci. 1976, 60, 365–384.
(5) Poelsema, B.; Machtberger, G.; Comsa, G. The Interaction of Hydrogen with Platinum(s)-9(111) × (111) Studied with Helium Beam Diffraction. Surf. Sci. 1981, 111, 519–544.
(6) Gee, A. T.; Hayden, B. E.; Dormke, C.; Nunney, T. S. The Role of Steps in the Dynamics of Hydrogen Dissociation on Pt(533). J. Chem. Phys. 2000, 112, 7660–7668.
(7) Groot, I. M. N.; Schouten, K. J. P.; Kleyn, A. W.; Juurlink, L. B. F. Dynamics of Hydrogen Dissociation on Stepped Platinum. J. Chem. Phys. 2008, 129, 224707.
(8) Groot, I. M. N.; Kley, A. W.; Juurlink, L. B. F. The Energy Dependence of the Ratio of Step and Terrace Reactivity for H₂ Dissociation on Stepped Platinum. Angew. Chem. 2011, 50, 5174–5177.
(9) Dahl, S.; Logadottir, A.; Eggeberg, R. C.; Larsen, J. H.; Chorkendorff, I.; Tønqvist, E.; Nørskov, J. K. Role of Steps in N₂ Activation on Ru(0001). Phys. Rev. Lett. 1999, 83, 1814–1817.
(10) Honkala, K.; Hellman, A.; Remediakis, I. N.; Logadottir, Á.; Carlson, A.; Dahl, S.; Christensen, C. H.; Nørskov, J. K. Ammonia Synthesis from First-Principles Calculations. Science 2005, 307, 555–558.
(11) Gee, A. T.; Hayden, B. E.; Dormke, C.; Kleyn, A. W.; Riedmüller, B. The Dynamics of the Dissociative Adsorption of Methane on Pt(533). J. Chem. Phys. 2003, 118, 3334–3341.
(12) Migliorini, D.; Chadwick, H.; Nattino, F.; Gutiérrez-González, A.; Dombrowski, E.; High, E. A.; Guo, H.; Utz, A. L.; Jackson, B.; Beck, R. D.; et al. Surface Reaction Barriermetry: Methane Dissociation on Flat and Stepped Transition-Metal Surfaces. J. Phys. Chem. Lett. 2017, 8, 4177–4182.
(13) Olsen, R. A.; McCormack, D. A.; Baerends, E. J. How Molecular Trapping Enhances the Reactivity of Rough Surfaces. Surf. Sci. 2004, 571, L325–L330.
(14) McCormack, D. A.; Olsen, R. A.; Baerends, E. J. Mechanisms of H₂ dissociative adsorption on the Pt(211) stepped surface. J. Chem. Phys. 2005, 122, 194708.
(15) Luppi, M.; McCormack, D. A.; Olsen, R. A.; Baerends, E. J. Rotational effects in the dissociative adsorption of H₂ on the Pt(211) stepped surface. J. Chem. Phys. 2005, 123, 164702.
(16) Ludwig, J.; Vlachos, D. G.; van Duijn, A. C. T.; Goddard, W. A. Dynamics of the Dissociation of Hydrogen on Stepped Platinum Surfaces using the ReaxFF Reactive Force Field. J. Phys. Chem. B 2006, 110, 4274–4282.
(17) Olsen, R. A.; McCormack, D. A.; Luppi, M.; Baerends, E. J. Six-dimensional quantum dynamics of H₂ dissociative adsorption on the Pt(211) stepped surface. J. Chem. Phys. 2008, 128, 194715.
(18) Füchsel, G.; Cao, K.; Er, S.; Smeets, E. W. F.; Kleyn, A. W.; Juurlink, L. B. F.; Kroes, G.-J. Anomalously Fast Dissociation on the Presence of Steps: Dissociation of D₂ on Cu(111). J. Phys. Chem. Lett. 2018, 9, 170–175.
(19) Cao, K.; Füchsel, G.; Kleyn, A. W.; Juurlink, L. B. F. Hydrogen Adsorption and Desorption from Cu(111) and Cu(211). Phys. Chem. Chem. Phys. 2018, 20, 22477–22488.
(20) Huang, X.; Yan, X. H.; Xiao, Y. Effects of vacancy and step on dissociative dynamics of H₂ on Pd (111) surfaces. Chem. Phys. Lett. 2012, 531, 143–148.
(21) Fuhrmann, T.; Kinne, M.; Tränkenschuh, B.; Papp, C.; Zhu, J. F.; Denecke, R.; Steinrück, H. P. Activated adsorption of methane on Pt(111)-an in situ XPS study. New J. Phys. 2005, 7, 107.
(43) Karplus, M.; Porter, R. N.; Sharma, R. D. Exchange Reactions with Activation Energy. I. Simple Barrier Potential for (H, H2). J. Chem. Phys. 1965, 43, 3259–3287.
(44) Füchsle, G.; del Cueto, M.; Díaz, C.; Kroes, G.-J. Enigmatic HCl + Au(111) Reaction: A Puzzle for Theory and Experiment. J. Phys. Chem. C 2016, 120, 25760–25779.
(45) Head-Gordon, M.; Tully, J. C. Molecular Dynamics with Electronic Friction. J. Chem. Phys. 1995, 103, 10317–10315.
(46) Lemos, D. S.; Gythiel, A. Paul Langevin’s 1908 paper “On the Theory of Brownian Motion” [“Sur la théorie du mouvement brownien,” C. R. Acad. Sci. (Paris) 146, 530–533 (1908)]. Am. J. Phys. 1997, 65, 1079–1081.
(47) Füchsle, G.; Klamroth, T.; Monturet, S.; Saalfrank, P. Dissipative dynamics within the electronic friction approach: the femtosecond laser desorption of H2/D2 from Ru(0001). Phys. Chem. Phys. 2011, 13, 8659–8670.
(48) Juaristi, J. I.; Alducin, M.; Muñoz, R. D.; Busnengo, H. F.; Salin, A. Role of Electron-Hole Pair Excitations in the Dissociative Adsorption of Diatomic Molecules on Metal Surfaces. Phys. Rev. Lett. 2008, 100, 116102.
(49) Novko, D.; Blanco-Rey, M.; Alducin, M.; Juaristi, J. I. Surface Electron Density Models for Accurate Ab Initio Molecular Dynamics with Electronic Friction. Phys. Rev. B 2016, 93, 245435.
(50) Paska, M. J.; Nieminen, R. M. Atoms Embedded in an Electron Gas: Phase Shifts and Cross Sections. Phys. Rev. B 1983, 27, 6121–6128.
(51) Füchsle, G.; Schimka, S.; Saalfrank, P. On the Role of Electronic Friction for Dissociative Adsorption and Scattering of Hydrogen Molecules at a Ru(0001) Surface. J. Phys. Chem. A 2013, 117, 8761–8769.
(52) Luntz, A. C.; Makkonen, I.; Persson, M.; Holloway, S.; Bird, D. M.; Mizieliński, M. S. Comment on “Role of Electron-Hole Pair Excitations in the Dissociative Adsorption of Diatomic Molecules on Metal Surfaces”. Phys. Rev. Lett. 2009, 102, 109601.
(53) Spiering, F.; Meyer, J. Testing Electronic Friction Models: Vibrational De-excitation in Scattering of H2 and D2 from Cu(111). J. Phys. Chem. Lett. 2018, 9, 1803–1808.
(54) Maurer, R. J.; Jiang, B.; Guo, H.; Tully, J. C. Mode Specific Electronic Friction in Dissociative Chemisorption on Metal Surfaces: H2 on Ag(111). Phys. Rev. Lett. 2017, 118, 256001.
(55) Kosloff, R. Time-Dependent Quantum-Mechanical Methods for Molecular Dynamics. J. Phys. Chem. 1988, 92, 2087–2100.
(56) Piiper, E.; Kroes, G. J.; Olsen, R. A.; Baerends, E. J. Reactive and diffractive scattering of H2 from Pt(111) studied using a six-dimensional wave packet method. J. Chem. Phys. 2002, 117, 5885–5898.
(57) Feit, M. D.; Fleck, J. A.; Steiger, A. Solution of the Schrödinger equation by a spectral method. J. Comput. Phys. 1982, 47, 412–433.
(58) Yibok, A.; Balint-Kurti, G. G. Parameterization of Complex Absorbing Potentials for Time-Dependent Quantum Dynamics. J. Phys. Chem. 1992, 96, 8712–8719.
(59) Corey, G. C.; Lemoine, D. Pseudospectral method for solving the time-dependent Schrödinger equation in spherical coordinates. J. Chem. Phys. 1992, 97, 4115–4126.
(60) Lemoine, D. The Finite Basis Representation as the Primary Space in Multidimensional Pseudospectral Schemes. J. Chem. Phys. 1994, 101, 10526–10532.
(61) Balint-Kurti, G. G.; Dixon, R. N.; Marston, C. C. Grid methods for solving the Schrödinger equation and time dependent quantum dynamics of molecular photofragmentation and reactive scattering processes. Int. Rev. Phys. Chem. 1992, 11, 317–344.
(62) Lettner, C. T.; Michelsen, H. A.; Auerbach, D. J. Quantum-state-specific dynamics of the dissociative adsorption and associative desorption of H2 at a Cu(111) surface. J. Chem. Phys. 1995, 102, 4625–4641.
(63) Ermak, D. L.; Buckholz, H. Numerical Integration of the Langevin Equation: Monte Carlo Simulation. J. Comp. Physiol. 1980, 35, 169–182.
(64) Winkler, A. Interaction of Atomic Hydrogen with Metal Surfaces. Appl. Phys. A 1998, 67, 637–644.
(65) Kroes, G.-J.; Pavanello, M.; Blanco-Rey, M.; Alducin, M.; Auerbach, D. J. Ab initio Molecular Dynamics Calculations on Scattering of Hyperthermal H Atoms from Cu(111) and Au(111). J. Chem. Phys. 2014, 141, 054705.
(66) Darling, G. R.; Holloway, S. Translation-to-vibrational excitation in the dissociative adsorption of D2. J. Chem. Phys. 1992, 97, 734–736.
(67) Polanyi, J. C. Concepts in Reaction Dynamics. Acc. Chem. Res. 1972, 5, 161–168.
(68) Gross, A.; Scheffler, M. Steering and Isotope Effects in the Dissociative Adsorption of H2/Pd(100). Frontiers in Materials Modelling and Design; Springer: Berlin, Heidelberg, 1998; pp 285–292.
(69) Busnengo, H. F.; Piiper, E.; Somers, M. F.; Kroes, G. J.; Salin, A.; Olsen, R. A.; Lemoine, D.; Dong, W. Six-dimensional quantum and classical dynamics study of H2 ( v = 0, J = 0) scattering from Pd(111). Chem. Phys. Lett. 2002, 356, 515–522.
(70) Gallagher, R. J.; Fenn, J. B. Rotational Relaxation of Molecular Hydrogen. J. Chem. Phys. 1974, 60, 3492–3499.
(71) Rendulic, K. D.; Anger, G.; Winkler, A. Wide range nozzle beam adsorption data for the systems H2/nickel and H2/Pd(100). Surf. Sci. 1989, 208, 404–424.
(72) Goikoetxea, I.; Juaristi, J. I.; Alducin, M.; Muñoz, R. D. Dissipative effects in the dynamics of N2 on tungsten surfaces. J. Phys.: Condens. Matter 2009, 21, 264007.