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The effect of corrugation on the quantum dynamics of dissociative and diffractive scattering of H_2 from Pt(111)

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We present results of two dimensional (2D) and three dimensional (3D) calculations for dissociative and diffractive scattering of H_2 from Pt(111), using a potential energy surface obtained from density functional theory (DFT) employing the generalized gradient approximation (GGA) in conjunction with a slab representation of the metal surface. The present study is motivated by the importance of Pt as a hydrogenation catalyst, and by a paradox regarding the amount of corrugation of the H_2 +Pt(111) potential energy surface (PES). Molecular beam experiments on dissociation of D_2 from a Pt(111) surface suggest a rather corrugated PES, which is at odds with results from molecular beam experiments on rotationally inelastic diffraction of HD from Pt(111), where only very little diffraction is found, suggesting a weakly corrugated PES. Results of our 3D calculations for off-normal incidence show that the present 3D model does not obey normal energy scaling, and that parallel motion inhibits dissociation at low collision energies, in agreement with the dissociation experiment. On the other hand, substantial diffraction is found, where the diffraction experiment found almost none. For each impact site considered in the 2D calculations, the computed dynamical barrier height, E_0 , is substantially lower than the barrier height in the PES, E_b , at that site. Both the 2D and the 3D calculations show a large vibrational enhancement of reaction. These effects are not due to a reduced mass effect, the barrier to dissociation being early, but to a decrease in the force constant of the H_2 vibration upon approaching the barrier to dissociative adsorption from the gas phase. The vibrational enhancement computed for H_2 +Pt(111) was not observed in seeded beam experiments on D_2 +Pt(111) [A. C. Luntz, J. K. Brown, and M. D. Williams, *J. Chem. Phys.* **93**, 5240 (1990)]. However, an analysis performed here strongly suggests that seeded beam experiments will be unable to observe vibrational enhancement if the dissociation of the molecule in $v=0$ proceeds without an energetic threshold, as is the case for H_2 +Pt(111). © 2000 American Institute of Physics. [S0021-9606(00)70442-9]

I. INTRODUCTION

Because of the central role of Pt as catalyst in hydrogenation reactions,¹⁻³ the interaction of H_2 (and its isotopes) with Pt surfaces has received much attention over the years. Conflicting views arose on the dissociation of H_2 on a Pt surface, a process of obvious importance for the understanding of platinum's activity as a hydrogenation catalyst. Considerable debate has been going on over the question what precisely the probability for dissociation is at the flat surface (terraces) and whether defects or steps were the main or only sites where dissociation occurs.¹⁻⁸

A vast amount of experimental studies of the H_2 +Pt system is available in the literature. For the present work, experiments on the dynamics of reactive and inelastic scattering⁴⁻²³ are the most relevant. The H_2 +Pt system has also received much theoretical attention. Among the theoretical work, electronic structure calculations²⁴⁻³³ prevail. Only a few studies are devoted to calculations on the dynamics.³⁴⁻⁴⁰ The calculations presented here are the first calculations on the quantum dynamics of dissociation of H_2 on Pt(111) using a potential energy surface (PES) obtained

using the generalized gradient approximation (GGA) of density functional theory (DFT).

The principal motivation for this study is a paradox concerning the amount of corrugation of the PES of the H_2 /Pt(111) system. This paradox arises from an apparent conflict between an experiment by Cowin *et al.*¹³ on rotationally inelastic and diffractive scattering of HD from Pt(111) and an experiment by Luntz *et al.*¹⁸ on dissociative chemisorption of D_2 on Pt(111).

In the experiment by Cowin *et al.*,¹³ rotationally inelastic and diffractive scattering probabilities were measured for an HD beam colliding with a Pt(111) surface. The measurements were done for an azimuthal angle of incidence corresponding to the $\langle 10\bar{1} \rangle$ direction of the crystal. The polar angle of incidence θ_i was varied from 25° to 85° in steps of 5°, $\theta_i=0$ corresponding to normal incidence. The angular distributions that were measured showed large probabilities for specular reflection in conjunction with rotational transitions $j=0 \rightarrow j' \neq j$, j being the angular momentum quantum number of HD. The angular distributions showed only weak diffraction probabilities, indicating a weakly corrugated PES.

In the experiment by Luntz *et al.*,¹⁸ the dissociative chemisorption probability at zero surface coverage, S_0 , was measured for D₂ on Pt(111) as function of initial translational energy. Measurements were done for a polar angle of incidence θ_i varying between 0° and 60°. The measurements showed a rapid falloff in the dissociation probability with increasing θ_i at all energies. The results also showed that normal energy scaling was not obeyed. [In case of normal energy scaling the probability for dissociation only depends on the normal component E_n of the initial translational energy E_i , i.e., $S_0(\theta_i, E_i) = S_0(E_n = E_i \cos^2 \theta_i)$.] The conclusion was that parallel translational energy has an important effect on dissociation of D₂ on Pt(111). But parallel translational energy is likely to have an effect *only if the PES is corrugated*, whereas the experiment by Cowin *et al.* suggested an *uncorrugated* PES. This defines the paradox alluded to above.

Another interesting result obtained by the group of Luntz was that there seemed to be no energetic threshold for dissociation of D₂ on Pt(111). Furthermore, for normal incidence they did not find any measurable difference between dissociation of H₂ and D₂. By investigating the dependence of dissociation on the nozzle temperature for a constant initial translational energy E_i , they concluded that vibrational enhancement of reaction was nonexistent for dissociation of D₂ on Pt(111). This finding is less obvious than one might think, theoretical work on unactivated and weakly activated reactions showing that these reactions may be vibrationally enhanced in spite of the barrier being absent or early.^{41,42}

From density functional theory (DFT) calculations,⁴³ we know that the PES for H₂/Pt(111) is both energetically and geometrically corrugated. (Energetic corrugation refers to the barrier height varying across the unit cell, the distance to the surface at which the barrier is located being constant. If, on the other hand, the distance to the surface at which the barrier is located varies across the unit cell, but the barrier height is constant, we speak of geometric corrugation.⁴⁴) For H₂/Pt(111), the barrier height varies from 0.06 eV for the top site to 0.42 eV for the fcc site. Although the barriers are all located in the entrance channel, there is still a substantial variation in their location, from $Z = 3.21$ to $Z = 4.25$ bohr.

The main goal of this paper is to study the effect of corrugation on dissociation and diffraction of H₂ from a Pt(111) surface. To this end calculations have been done for normal and off-normal incidence. In the present study we use a three dimensional (3D) model. The model treats the surface atoms as static and assumes that scattering occurs on a single PES. The molecular degrees of freedom are (1) motion of the center of mass normal to the surface, (2) motion in the H–H distance r , and (3) motion of the molecule along one axis parallel to the surface. The molecule has a fixed orientation such that its bond axis is always parallel to the surface.

The motion in all three degrees of freedom is treated fully quantum mechanically. The calculations are performed using a time-dependent wave packet (TDWP) method. The 3D PES used in the dynamics calculations is an analytical interpolation of four 2D PESs obtained from DFT calculations,⁴³ as described below. We also present results of

FIG. 1. Coordinate system used to describe H₂ interacting with a Pt(111) surface. The encircled coordinates represent the degrees of freedom of H₂ in the present 3D calculations. The X-axis is chosen as shown in Fig. 2.

two dimensional (2D) calculations in which the molecule remains fixed over a particular site.

This paper is organized as follows. In Sec. II A the wave packet method and propagation method used are discussed. The interpolation of the four 2D PESs to obtain a 3D PES is described in Sec. II B. Section II C presents some computational details. In Sec. III results from 2D and 3D calculations are presented. Section IV concludes.

II. THEORY

A. The TDWP method and the dynamical model

The dissociation of H₂ on a Pt(111) surface is described within a 3D model. In this model, the surface atoms are fixed to their ideal positions (i.e., the equilibrium positions they occupy in the crystal), and the Born–Oppenheimer approximation is used to constrain the scattering to occur on a single PES. The molecule has in total six degrees of freedom with respect to the surface. These are schematically shown in Fig. 1. In the present 3D model, the molecular motion parallel to the surface is restricted to one degree of freedom, which will be called X. The X-axis is chosen as shown in Fig. 2. It is chosen such that it connects the two top sites that lie furthest apart within the (111) unit cell. The distance between two neighboring top sites along this X-axis is 9.07 bohr. This quantity will be called the lattice constant and denoted by the letter L .

FIG. 2. Top view of the Pt(111) surface. The unit cell is indicated by a diamond shaped line connecting four top sites. The X-axis is chosen as shown. The distance between two neighboring top sites along the X-axis is 9.07 bohr. The dumbbell on top represents the H₂ molecule whose orientation is fixed at $\theta = 90^\circ$ and $\phi = 90^\circ$ (the angles θ and ϕ are defined in Fig. 1). The relative sizes of the atoms are exaggerated for illustrative purposes.

The other two degrees of freedom are the distance of the molecule's center of mass to the surface, Z , and the H–H distance, r . The orientation of the molecule is fixed at $\theta=90^\circ$ and $\phi=90^\circ$, so that the molecular bond is parallel to the surface and perpendicular to the X -axis (see Fig. 2). The Hamiltonian corresponding to this 3D model is given by

$$\hat{H} = -\frac{1}{2M} \frac{\partial^2}{\partial Z^2} - \frac{1}{2M} \frac{\partial^2}{\partial X^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + V_{3D}(Z, X, r), \quad (1)$$

where atomic units have been used. In the above expression for the Hamiltonian, M and μ are the total and reduced mass of H_2 , respectively. V_{3D} represents the 3D interaction potential of the two H atoms with each other and with the metal surface. For large Z , V_{3D} reduces to the gas phase H_2 potential.

The interaction potential is an analytical fit of four 2D PESs obtained from electronic structure calculations.⁴³ The potential and the particular interpolation procedure used will be discussed in Sec. II B.

The wave function is represented on a grid in Z , X , and r using a direct product discrete variable representation (DVR) (Ref. 45) with constant grid spacings ΔZ , ΔX , and Δr . The scattering of H_2 from Pt(111) is treated in a time-dependent formulation. The solutions at time $t + \Delta t$ and time t are related by

$$\Psi(Z, X, r; t + \Delta t) = \exp(-i\hat{H}\Delta t)\Psi(Z, X, r; t). \quad (2)$$

Equation (2) defines an initial value problem. The calculation starts with an initial wave packet which is located far from the surface such that its interaction with the surface is negligible. Its initial form is taken to be

$$\Psi(Z, X, r; t=0) = \chi_{\nu_0}(r) \frac{\exp(iK_X^0 X)}{\sqrt{L}} \int_{-\infty}^{\infty} dk_z b(k_z) \frac{\exp(ik_z Z)}{\sqrt{2\pi}}, \quad (3)$$

where K_X^0 is the molecule's initial translational momentum in X . The molecule's initial vibrational state is defined by the quantum number ν_0 , and is described by the wave function χ_{ν_0} . A Gaussian distribution, $b(k_z)$, is used to define the motion in Z of the initial wave packet.⁴⁶

Equation (2) is implemented using the split operator propagation (SPO) method.⁴⁷ Here, the kinetic energy operator $\hat{K}$ and interaction potential V are assumed to commute, so that we can write

$$\exp(-i\hat{H}\Delta t) = \exp(-i\hat{K}\Delta t/2) \exp(-iV\Delta t) \exp(-i\hat{K}\Delta t/2), \quad (4)$$

where Δt represents the size of the time step with which the wave function is propagated forward in time. The leading error per time step in this approximation is proportional to Δt^3 .^{47,48}

Operations of $\hat{K}$ and V on the wave function are carried out in a local representation. The evaluation of $\hat{K}$ on the wave function proceeds by first transforming the wave function to momentum space using a fast 3D Fourier transformation (FFT),^{47,49} and then multiplying at each grid point by $\exp(-i\hat{K}(p_Z^i, p_r^j, p_X^k)\Delta t/2)$. The wave function is then transformed back to coordinate space by an inverse FFT to evalu-

ate the action of $\exp(-iV(Z_i, r_j, X_k)\Delta t)$ on the wave function. The propagation over one time step is then completed by another FFT to momentum space followed by the application of $\exp(-i\hat{K}\Delta t/2)$.

Elastic and inelastic scattering probabilities are obtained using a formalism developed by Balint-Kurti *et al.*^{50–52} In this formalism a dividing surface is placed at $Z=Z_\infty$ beyond which the molecule-surface interaction is negligible. Every Δt_A , the scattered wave function is analyzed at the dividing surface. Note: Δt_A should be taken smaller than $\pi/\Delta E$, ΔE being the range of collisions energies contained in the initial wave packet, to avoid potential problems with aliasing. The value of Δt_A for which converged results are obtained will usually be much larger than the time step used in the propagation. The analysis includes taking the overlaps of the scattered wave function with the asymptotic states to obtain the S -matrix elements. The S -matrix elements are related to transition probabilities according to $P_{if} = |S_{if}|^2$, where i and f correspond to an initial (asymptotic) state defined by Eq. (3) and a final (asymptotic) state, respectively. Initial state resolved reaction probabilities are then obtained as

$$R_\nu = 1 - \sum_{\nu'n} P(\nu \rightarrow \nu'n), \quad (5)$$

where ν and ν' refer to the initial and final vibrational state, respectively. The quantum number n is the diffraction quantum number for diffraction along X . The summation is taken over all energetically accessible gas-phase states.

The part of the wave function that has been analyzed and travels beyond Z_∞ is no longer needed and, therefore, gradually absorbed using an optical potential of the form,⁵³

$$V_{\text{abs}}(Z) = \begin{cases} -iA_2 \left(\frac{Z - Z_{\text{min}}}{Z_{\text{max}} - Z_{\text{min}}} \right)^2 & \text{if } Z_{\text{min}} \leq Z \leq Z_{\text{max}}, \\ 0 & \text{if } Z < Z_{\text{min}}, \end{cases} \quad (6)$$

where a suitable choice for Z_{min} is $Z_{\text{min}} = Z_\infty$. Z_{max} is best taken as the last grid point in Z . The A_2 parameter in Eq. (6) should then be chosen to achieve efficient absorption for all energies contained in the scattered wave packet, while keeping the range over which the optical potential is defined minimal.

The molecule is considered to be dissociated for r larger than some value r_d . For values of $r > r_d$, the wave function in r is absorbed using an optical potential $V_{\text{abs}}(r)$ similar to Eq. (6).

B. The PES

From electronic structure calculations,⁴³ four 2D PESs were obtained for $X=0$, $X=(1/6)L$, $X=(1/3)L$, and $X=(1/2)L$, where $X=0$ corresponds to a bridge site and $X=(1/2)L$ to a top site (see Fig. 2). Using these four 2D PESs, a 3D PES was constructed. The procedure used is based on the assumption that $V(Z, r, X=aL) = V(Z, r, X=(1-a)L)$, for $0 \leq a \leq 1$. Electronic structure calculations performed for the H_2 orientation shown in Fig. 2, and for $X=(1/3)L$ and $X=(2/3)L$ showed that this approximation is quite reasonable.⁴³

FIG. 3. Contour plots of four 2D PES computed by DFT and used to fit the 3D PES V^I . The level spacing is 0.1 eV. The height, E_b , and distance from the surface, Z_b , of each barrier are indicated in the plot.

In Fig. 3 contour plots of the computed 2D PESs are shown. Each 2D PES is a bicubic spline fit to between 50–60 potential points computed by DFT. Indicated in each plot is the barrier height E_b (with respect to the gas-phase) and the barrier location Z_b . Moving along the X -axis, the barrier height and barrier location vary from 0.06 eV to 0.42 eV, and from $3.21 a_0$ to $4.25 a_0$, respectively. Therefore, the PES along X is both energetically and geometrically corrugated.

At first, a 3D PES, V^I , in the coordinates Z , X , and r was constructed by interpolating the four 2D PESs from Fig. 3, using the following analytical expression:

$$V^I(Z, r, X) = C_0(Z, r) + C_1(Z, r)\cos(kX) + C_2(Z, r)\cos(2kX) + C_3(Z, r)\cos(3kX), \quad (7)$$

where $k = 2\pi/L$. Four equations can now be set up, one for each value of X for which the 2D PES is known. Expressions for the coefficients C_0 , C_1 , C_2 , and C_3 in terms of the four 2D PESs known can then be obtained by solving a set of linear equations.

Using the procedure described above, an artifact appears in the exit channel for values of X close to $X = (1/4)L$ (see upper plot in Fig. 4). Figure 5 is a 1D cut for values of Z and r far beyond the barrier ($Z = 1.8$, $r = 2.0$). For these particular values of Z and r the potential difference between $X = (1/4)L$ and $(1/2)L$ is largest. At $X = (1/4)L$ a deep well is seen to exist. Figure 5 suggests that the artificial well is due to the use of a high order interpolant in X for a potential that is quite corrugated at the (Z, r) values for which the artifact occurs. Inspection of the dependence of the potential on Z , r and X showed that the artifact in Fig. 4 is in fact an *absolute minimum* in V^I . Figure 5 also suggests a remedy: the X -dependence of the potential between $X = (1/6)L$ and

FIG. 4. Contour plots for $X = (1/4)L$ are shown. The 2D PES in the upper plot is a cut through V^I . It shows an artifact in the exit channel. The 2D PES in the lower plot is a cut through V^{III} .

$(1/3)L$ can be changed by changing one of the 2D PES on which the interpolation is based in such a way that the artificial well disappears, at the same time making sure that new artefacts do not appear somewhere else. This should be done in the region beyond the barrier to ensure that the dissociation dynamics is not affected by this procedure. Raising the potential in the region beyond the barrier for $X = (1/6)L$ produced the desired effect.

The raising of the potential for $X = (1/6)L$ was performed as follows: First, the 2D PESs for $X = 0$ and $X = (1/2)L$ were interpolated using

$$V^{II}(Z, r, X) = C_0(Z, r) + C_1(Z, r)\cos(kX). \quad (8)$$

In Fig. 5, one can see that the potential in the exit channel for $X = (1/6)L$ is always larger for V^{II} than for V^I . From V^{II} we obtain an interpolated 2D PES for $X = (1/6)L$, which will be referred to as $V_{1/6}^*$. The 2D PES for $X = (1/6)L$ from V^I will be referred to as $V_{1/6}$.

We now define a shifted 2D PES $V_{1/6}^S$ as

$$V_{1/6}^S(Z, r) = F_S(Z) * V_{1/6}(Z, r) + (1 - F_S(Z)) * V_{1/6}^*(Z, r). \quad (9)$$

FIG. 5. One-dimensional cuts through the interaction potential for $Z=1.8a_0$ and $r=2.0a_0$. The solid line is the result of an interpolation based on four 2D PESs (V^I). The dashed line is the result of an interpolation based on the same four 2D PESs, but with the potential beyond the barrier for $X=(1/6)L$ shifted upwards (V^{III}). The dotted line is the result of an interpolation based on the 2D PESs for $X=0$ and $X=(1/2)L$ only (V^{II}). The $\times$ -symbols indicate the points on which the interpolations are based.

This shifted 2D PES $V_{1/6}^S$ is then used to replace $V_{1/6}$ in the expressions for the coefficients appearing in Eq. (7). The resulting 3D PES is called V^{III} , to distinguish it from V^I .

F_S is a switching function and is defined as

$$F_S(Z) = \begin{cases} 1 & \text{if } Z > Z_{\max} \\ 0 & \text{if } Z < Z_{\min} \\ \frac{1}{2} - \frac{1}{2} \cos\left(\pi \frac{Z - Z_{\min}}{Z_{\max} - Z_{\min}}\right) & \text{if } Z_{\min} < Z < Z_{\max}, \end{cases} \quad (10)$$

where $Z_{\max}=2.5$ bohr and $Z_{\min}=1.5$ bohr was used. For values of $Z > Z_{\max}$, $V_{1/6}^S$ is equal to $V_{1/6}$. This means we can ensure that the potential before and a little beyond the barrier is not affected by the switching procedure, which is a crucial point. For values of $Z < Z_{\min}$, $V_{1/6}^S$ is equal to $V_{1/6}^*$. Although the potential in the exit channel has been modified by the switching procedure, it is expected that this hardly influences the actual dissociation process in which we are interested. That this is indeed the case will be shown below in Sec. III.

In Fig. 4, cuts through the interpolated 3D PESs are shown for $X=(1/4)L$. The upper 2D PES is a cut through V^I , the lower 2D PES through V^{III} . The 2D PES in the lower plot no longer suffers from an artifact in the exit channel. Dissociation probabilities for the 2D PESs in Fig. 4 will be compared in Sec. III.

C. Computational details

Numerical values of the parameters used in the 3D calculations for normal incidence ($\theta_i=0$) of $\nu=0$ H_2 are given in Table I. Calculations were done for $\nu=0$ H_2 , $\nu=1$ H_2 , and $\nu=0$ D_2 , in both 2D and 3D and for the three energy ranges 0.05–0.15 eV, 0.15–0.25 eV, and 0.25–0.50 eV. Three initial wave packets are used rather than one because a wave packet that would span the total energy range 0.05–0.50 eV

TABLE I. Number values for the input parameters used in the 3D calculation on dissociation of $\nu=0$ H_2 for the energy ranges indicated. Parameter values are in atomic units unless indicated otherwise.

Parameter	Energy range eV		
	[0.05–0.15]	[0.15–0.25]	[0.25–0.50]
Initial wave packet			
Width ξ (bohr)	1.460	2.043	1.149
Initial position Z_0	11.0	same	same
Average initial momentum k_{z0}	5.013	7.284	9.911
Grid parameters			
Z_i	–1.0	same	same
N_z	180	same	same
r_i	0.4	same	same
N_r	54	64	64
N_x	60	same	same
N_Z^p , # grid points specular grid	240	same	same
Grid spacing ΔZ	0.10	same	same
Grid spacing ΔX	0.151	same	same
Grid spacing Δr	0.15	same	same
Lattice constant L	9.07	same	same
Time propagation			
Size time step Δt	2.5	same	same
Number of time steps	40 000	12 000	12 000
Optical potential in Z			
Initial value of range $Z_{\min}$	11.80	same	same
Proportionality constant A_2 (eV)	0.0034	0.0041	0.0041
Range L_0	5.1	same	same
Optical potential in r			
Initial value of range r_d	5.35	same	same
Proportionality constant A_2 (eV)	0.023	0.0094	0.0094
Range L_0	3.0	4.5	4.5
Other parameters			
Size time step analysis Δt_A	50	same	same
Analysis value Z_∞	11.80	same	same

would contain translational momenta close to zero, which would present various computational difficulties.

A time step of $\Delta t=2.5$ a.u. was required to obtain converged results for $\nu=0$ H_2 and D_2 . For $\nu=1$ H_2 a time step of $\Delta t=1.0$ a.u. was needed.

For $\nu=0$ H_2 , grid spacings in Z and r of $\Delta r=0.15$ bohr and $\Delta Z=0.10$ bohr were used, respectively. The grid spacings used in the calculations for $\nu=1$ H_2 were $\Delta Z=0.10$ bohr and $\Delta r=0.10$ bohr, and $\Delta Z=0.07$ bohr and $\Delta r=0.10$ bohr were used for $\nu=0$ D_2 . The grids started at $Z_i=-1.0$ bohr and $r_i=0.4$ bohr, in all calculations.

Optical potentials in r were needed that acted over quite a large range, the reason being that the $H_2/Pt(111)$ system is an early barrier system. Model calculations by Halstead and Holloway⁵⁴ have shown that for an early barrier system, the reaction product's vibrational motion with respect to the surface can be highly excited. Therefore, the kinetic energies in r are spread out over a large range, requiring the use of an optical potential that extends over a large range in r to efficiently absorb the outgoing wave packet.

To reduce the grid size in Z , use was made of the projection operator formalism⁵⁵ to bring in the initial wave packet on an separate grid in Z and r .

For off-normal incidence, the same values for the parameters were used as for normal incidence, with the exception of the number of grid points in X and the time step Δt . For

FIG. 6. Shown is the 2D dissociation probability as function of the incident translational energy E_z for scattering of initial $\nu=0$ H₂, for four different surface sites.

an incidence angle equal to 60° , $N_X=96$ was used. For an incidence angle equal to 45° , $N_X=80$ was used. For incidence angles lower than 45° , $N_X=60$ was used. For all off-normal incidence angles, $\Delta t=2.0$ a.u. was used.

With the choice of parameters as described above, all probabilities greater than 0.05 were converged to within 1% of their absolute value, whereas probabilities between 0.01 and 0.05 were converged to within 2%.

III. RESULTS AND DISCUSSION

Results obtained for dissociative and diffractive scattering are presented and discussed. In Sec. III A results of 2D calculations are given. In Sec. III B results of 2D wave packet calculations on differently interpolated PESs are compared. Section III C presents results of 3D calculations for normal and off-normal incidence.

A. 2D model

In the 2D model the H₂ molecule is constrained to move above a fixed site. Calculations have been done for $X=0$, $(1/6)L$, $(1/3)L$, and $(1/2)L$. Figure 6 shows the dissociation probability as a function of the incidence translational energy normal to the surface E_z , for these four sites. From Fig. 3 it was already known that there is a large variation in the barrier height that the molecule sees as it moves along the X -axis. This is reflected in the dissociation curves lying far apart in Fig. 6.

In Table II the barrier height E_b in the PES is compared

TABLE II. Table of potential barrier height E_b vs dynamical barrier height E_0 for initial $\nu=0$, 1 H₂ and $\nu=0$ D₂, for $X=0$, $(1/6)L$, $(1/3)L$, and $(1/2)L$. All energies are in eV.

X/L	E_b	$E_0(\nu=0 \text{ H}_2)$	$E_0(\nu=1 \text{ H}_2)$	$E_0(\nu=0 \text{ D}_2)$
0	0.27	0.206	0.118	0.225
(1/6)	0.42	0.338	0.201	0.361
(1/3)	0.20	0.156	0.097	0.167
(1/2)	0.06	0.036	<0.02	0.043

FIG. 7. The 2D dissociation probability is plotted as function of the incident translational energy E_z for scattering of initial $\nu=0$ H₂ (R_0), $\nu=1$ H₂ (R_1) and $\nu=0$ D₂ (R_0, D_2), for $X=0$ and $X=(1/2)L$.

with the dynamical barrier height E_0 for these four sites. (The dynamical barrier height is defined as the translational energy E_z for which the dissociation probability first becomes half its saturation value, and as such it is a measure of the effective barrier the molecule experiences.) Not surprisingly, as a function of X , the energy ordering of E_0 follows that of E_b . What may seem surprising is that E_0 is much smaller than E_b for each of the four sites. This seems surprising because all the barriers are located in the entrance channel. Therefore, it is unlikely that E_0 should be lowered relative to E_b due to zero-point energy release through a reduced mass effect, as discussed in Ref. 54. An alternative way in which zero-point energy can be released in the entrance channel^{38–41} is discussed below.

Probabilities for dissociation of $\nu=1$ H₂ and $\nu=0$ D₂ are shown in Fig. 7, together with $\nu=0$ H₂ for reference. Results are presented for $X=0$ and $X=(1/2)L$. For both sites a small isotope effect is found. The effect is smallest for $X=(1/2)L$; the dynamical barrier height of $\nu=0$ D₂ is 0.006 eV higher than for $\nu=0$ H₂. For $X=0$, the dynamical barrier height of $\nu=0$ D₂ is 0.017 eV higher than for $\nu=0$ H₂ (see Table II). Also, an interesting effect is found for $X=(1/2)L$, where the dissociation curve for $\nu=0$ D₂ is seen to cross that for $\nu=0$ H₂ at approximately $E_z=0.05$ eV. This

FIG. 8. Shown is the potential V as function of r for $X=0$, and for the four values of Z indicated.

can be explained by the dissociation of D_2 behaving more classically than dissociation of H_2 , the dissociation curve for D_2 being less wide than for H_2 .⁵⁴ In the case that the onset of the dissociation curve for D_2 is shifted to higher energies relative to that of H_2 by less than the difference in their widths, the curves will cross.

Also, for both sites a large vibrational enhancement of reaction of H_2 is found. Again, these findings might at first seem contradictory with the fact that all the barriers are located in the entrance channel, where the reduced mass associated with the vibration perpendicular to the reaction path changes only very little as the molecule approaches the barrier. Calculations⁵⁴ on dissociative chemisorption of H_2 which used a model PES with barriers located in the entrance channel showed only a small vibrational enhancement of reaction, and a small isotope effect.

To understand our findings (E_0 substantially smaller than E_b for $\nu=0$ H_2 , large vibrational enhancement of reaction of H_2 , and an isotope effect), the potential along r in the entrance channel of the 2D PESs was studied more closely. In Fig. 8, the potential along r is plotted for four values of Z , for $X=0$. Figure 8 is also representative for other values of X . As the H_2 approaches the barrier, the H–H bond softens causing the vibrational frequency to decrease, and, therefore, also the zero-point energy. In this way zero-point energy is already released in the entrance channel even though the reduced mass associated with the motion perpendicular to the reaction path remains the same. For initial $\nu=1$ H_2 , the amount of vibrational energy that is released due to a decrease of the vibrational frequency is expected to be even larger (by a factor of 3) than the vibrational energy release of $\nu=0$ H_2 .

A decrease of the vibrational frequency as the molecule approaches the surface (and hence a decrease of the vibrational energy) was studied before by Müller,^{38–40} and Gross and Scheffler.⁴¹ Based on local density approximation (LDA) calculations, Müller predicted a decrease in the zero-point energy of H_2 upon approaching the Pt(111) surface. However, Müller did not point out one implication of the weak-

ening of the molecular bond noted here, i.e., that dissociation of H_2 on Pt(111) should be vibrationally enhanced. A decrease of the vibrational frequency of H_2 in the entrance channel was also observed by Gross and Scheffler for the nonactivated reaction of H_2 on Pd(100), and used to explain the vibrational enhancement of reaction they computed for this system, as well as the strong vibrational heating observed before in desorption experiments.

We analyzed the vibrational enhancement of reaction quantitatively in much the same way as was done for H_2 +Pd(100) by Gross and Scheffler.⁴¹ Full details are given elsewhere.⁴² Briefly, the potential is computed along the reaction path. From this we subtract the vibrational energy released as H_2 in its vibrational state ν moves in from the gas phase to a distance Z from the surface on the reaction path. The energy release is computed by solving the vibrational eigenvalue problem⁵⁶ for H_2 in the gas phase and at various distances Z along the reaction path. This way vibrationally adiabatic potentials are computed. Like the original potential, when plotted as a function of Z , these effective potentials display barrier heights, E_{eff}^ν , but these barrier heights are significantly lowered with respect to the barrier heights in the potential, due to the release of vibrational energy. For instance, for $X=0$, $E_{\text{eff}}^0 \approx 0.20$ and $E_{\text{eff}}^1 \approx 0.12$ eV. For $X=(1/6)L$, $E_{\text{eff}}^0 \approx 0.33$ and $E_{\text{eff}}^1 \approx 0.20$ eV. As Table II shows, the computed effective barrier heights correlate quite well with the dynamical barrier heights obtained from the wave packet calculations. This shows that, to a good approximation, the reactive motion over the barrier proceeds vibrationally adiabatically. It also shows that the vibrational energy release can be explained by a change in the force constant of H_2 ; the release is not due to a mass effect associated with a late barrier.

These results raise an interesting question: To what extent is the vibrational enhancement of reaction in late barrier systems [such as H_2 +Cu (Refs. 57, 58)] actually due to the decrease in the reduced mass associated with the vibration perpendicular to the reaction path, to which it is usually attributed? Does a decrease of the associated force constant perhaps also play an important role for such systems?

The isotope effect found can now also be understood qualitatively. Because D_2 has twice the reduced mass of H_2 , less zero-point energy will be released along Z . As a consequence D_2 experiences a larger effective barrier height.

B. Effect of modifying the PES for intermediate X

It will now be demonstrated that the modification made to the exit channel of the 2D PES for $X=(1/6)L$ has very little effect on the dynamics of the dissociation process at this site. In the upper plot of Fig. 9 dissociation probabilities are shown for the original and modified 2D PES for $X=(1/6)L$. Changing the potential in the exit channel is seen to have a negligible effect on the dissociation process, the two curves practically coinciding.

Using the modified 2D PES for $X=(1/6)L$ to fit a 3D PES proved to be successful in removing the artifact that appeared for the interpolated PES in the exit channel for values of X close to $X=(1/4)L$. 2D dissociation probabilities

FIG. 9. The 2D dissociation probability of initial $\nu=0$ H₂ as a function of the initial translational energy E_z is shown for $X=(1/6)L$ and $X=(1/4)L$. In the top panel results are plotted for the modified 2D PES $V_{1/6}^S$ (dashed line) and original 2D PES $V_{1/6}$ (solid line), for $X=(1/6)L$. The dashed line in the lower panel for $X=(1/4)L$ corresponds to V^I of Fig. 4. The solid line is the result of a calculation using V^{III} , also shown in Fig. 4.

calculated using the interpolated PESs V^I and V^{III} for $X=(1/4)L$ are shown in Fig. 9. The two curves shown correspond to the 2D PESs plotted in Fig. 4. The dashed line is the result of a calculation using the 2D PES with the artifact still in the exit channel. It is seen to possess a lot of structure which is ascribed to resonances due to the artificial well in the exit channel. It was anticipated that the artifact in the original interpolated PES would also lead to artificial resonances in 3D calculations for this PES. Figure 9 also shows the results of a 2D calculation using the interpolated PES for $X=(1/4)L$ with the artifact removed. A smooth reaction probability curve was obtained as expected.

In the 3D calculations V^{III} is used because it is expected that it will not give rise to artificial resonances in the reaction probabilities, and because the 2D results for $X=(1/6)L$ [for which the PES was actually calculated, but also changed in the exit channel to remove the artifact at $X=(1/4)L$] remained essentially unchanged.

C. 3D model

In the 3D model the H₂ molecule has one translational degree of freedom parallel to the surface, which means that

FIG. 10. The 3D dissociation probability for normal incidence as function of the initial translational energy E_z is plotted for scattering of initial $\nu=0$ H₂, $\nu=1$ H₂ and $\nu=0$ D₂.

diffractive scattering also comes in to play. Dissociation and diffraction probabilities were computed for various angles of incidence.

Figure 10 shows the dissociation probability for $\nu=0$ H₂, $\nu=1$ H₂ and $\nu=0$ D₂, for normal incidence. For energies as low as 0.05 eV already substantial dissociation probabilities are found for both $\nu=0$ H₂ ($P \approx 0.17$) and $\nu=0$ D₂ ($P \approx 0.12$), indicating that there is no or almost no threshold to dissociation for H₂ and D₂ on Pt(111) in the present 3D model. This result is in agreement with experiment.¹⁸

The reaction probabilities computed for normal incidence show a small isotope effect. At larger E_z , the reaction probability curve for $\nu=0$ D₂ is shifted relative to that of $\nu=0$ H₂ to higher E_z by about 0.02 eV, which is approximately the difference in the computed dynamical barrier heights E_0 : $E_0=0.206$ eV for $\nu=0$ H₂, and $E_0=0.225$ eV for $\nu=0$ D₂.

The 3D reaction probabilities computed for $\nu=0$ and $\nu=1$ H₂ at normal incidence also show a vibrational enhancement effect. For $\nu=0$ H₂, $E_0=0.206$ eV, and for $\nu=1$ H₂, $E_0=0.118$. Both the isotope effect and vibrational enhancement effect can be explained from the reduction in the force constant of the H₂ vibration as the molecule approaches the surface, as discussed in Sec. III A. Here, we only discuss how the computational findings compare with experiment.

In the molecular beam experiments of Luntz *et al.*¹⁸ no isotope effect was detected. However, the size of the isotope effect we found (0.017 eV) might be too small to have been observable in the experiments. It is also possible that the isotope effect is an artifact of the reduced dimensionality of our calculations. The lowering of the zero-point vibrational energy of H₂ approaching the barrier could well be matched by an increase in the zero-point energy associated with the rotational motion of H₂, due to the confinement of H₂ to a range of orientations close to parallel to the surface near the barrier, as first pointed out by Müller.^{39,40} If rotational and vibrational effects should (almost) cancel for H₂, the same

FIG. 11. The reaction probability S_0 of a fictitious molecular beam experiment is plotted for $\text{H}_2/\text{Cu}(100)$ (upper) and $\text{H}_2/\text{Pt}(111)$ (lower), for beam temperatures of 0 K (solid line) and 1800 K (dotted line). Also plotted is their ratio Q (dashed line). The results are shown as a function of the normal incidence energy, E_z .

would occur for D_2 . In this case, an isotope effect would probably not be observable.^{39,40}

In the seeded molecular beam experiment of Luntz *et al.*,¹⁸ vibrational energy was not found to enhance the reaction, whereas the present calculation shows a fairly large vibrational enhancement of reaction. In the experiment, the reaction probability was measured for nozzle temperatures, T_N , ranging from 300 K through 1800 K, for normal incidence and a fixed total incidence translational energy.^{59–61}

In Fig. 11, reaction probabilities, S_0 , for nozzles temperatures of 0 and 1800 K are compared for a weakly activated system (the one under present investigation) and a strongly activated system ($\text{H}_2 + \text{Cu}$ in this case). In the upper plot of Fig. 11, the reaction probability is plotted as it would be measured in a fictitious seeded molecular beam experiment on reaction of H_2 on $\text{Cu}(100)$. A Boltzmann distribution is assumed for the population of the vibrational energy levels of the H_2 molecules in the initial beam (neglecting contributions of $\nu=2$ and higher states). The reaction curves for $\nu=0$ and $\nu=1$, were taken according to the formula used by Michelsen and Auerbach.⁶² The lower plot of Fig. 11 shows the reaction curve that would be obtained in a similar experiment on $\text{H}_2 + \text{Pt}(111)$ based on the present calculations (again neglecting the contribution of $\nu=2$ and higher states). Also plotted in Fig. 11 is the ratio $Q = S_0(T_N = 1800\text{K})/S_0(T_N = 0\text{K})$, showing that increasing

the nozzle temperature in a seeded beam experiment on a strongly activated reaction, like H_2 on Cu , can lead to a large increase in the measured reaction probability $S_0(T_N)$. Seeded beam experiments are thus sensitive to vibrational enhancement for strongly activated reactions. On the other hand, even though there is significant vibrational enhancement of reaction on $\text{Pt}(111)$, the effect should be hard to measure in a seeded beam experiment, because the reaction of the predominantly populated $\nu=0$ state can proceed without an energetic threshold (i.e., the reaction probability is already of the order of 0.1 at low energies). This shows that seeded beam experiments may not be sensitive to vibrational enhancement of weakly activated reactions. This is all the more true because increasing the nozzle temperature will also increase the rotational temperature of the H_2 molecules. As has also been pointed out by Luntz *et al.*,¹⁸ this could lead to a cancellation of the (small) vibrational enhancement effect if the reaction is rotationally hindered at low j , as is the case for $\text{H}_2(\text{D}_2) + \text{Cu}(111)$.^{63,64}

To study the effect of incidence angle, the molecule was given initial momentum K_X^0 parallel to the surface. From one wave packet calculation, it is possible to extract results for a range of translational energies normal to the surface, E_z , but only for *one* value of K_X^0 ; as a result in such a calculation, the incidence angle θ_i varies with E_z according to

$$\tan^2 \theta_i = \frac{E_X^0}{E_z}, \quad (11)$$

where E_X^0 is the energy in motion parallel to the surface corresponding to the initial momentum K_X^0 . Obtaining results for one angle θ_i and for a range of energies normal to the surface is computationally unfavorable, because for each E_z a different value of K_X^0 (E_X^0) needs to be used, requiring many separate wave packet calculations. To save on computational time, instead of performing calculations for fixed θ_i , we perform calculations for fixed K_X^0 . However, to establish a connection with experiment in which the incident conditions are usually defined by specifying the incidence angles, K_X^0 is chosen to correspond to a particular value of θ_i at $E_z = E_0$, where E_0 is the dynamical barrier height for H_2 for normal incidence.

Calculations were done for five different initial momenta parallel to the surface, K_X^0 . The initial energy parallel to the surface, E_X^0 , corresponding to K_X^0 , was taken according to the definition

$$E_X^0 = E_0 \tan^2 \vartheta_i. \quad (12)$$

Equation (12) defines a one-to-one correspondence between the angle ϑ_i and the initial energy E_X^0 for $-\pi/2 \leq \vartheta_i \leq \pi/2$. The value of ϑ_i will be used for labeling, along with K_X^0 . If we put E_z equal to E_0 in Eq. (11), we obtain Eq. (12), indicating that for $E_z = E_0$ the angle of incidence θ_i is equal to the angle ϑ_i . Calculations were done for angles $\vartheta_i = 10^\circ, 20^\circ, 30^\circ, 45^\circ$, and 60° , corresponding to $K_X^0 = 1.32, 2.71, 4.31, 7.46$, and 12.91 a.u. For these values of K_X^0 , the initial energies in X vary from $E_X^0 = 0.00641$ eV for $\vartheta_i = 10^\circ$ to $E_X^0 = 0.618$ eV for $\vartheta_i = 60^\circ$.

Figure 12 shows the dissociation probabilities as function of the initial translational energy E_z for various angles

FIG. 12. The 3D dissociation probability for off-normal incidence as function of the normal incident translational energy, E_Z , is shown for different values of ϑ_i . The values of K_X^0 to which ϑ_i corresponds are given in atomic units.

of incidence. The reaction probability curves are clearly distinct, showing that the reaction probability also depends on E_X^0 . This result is in agreement with the results obtained by Luntz *et al.*,¹⁸ who also found that reaction of D₂ on Pt(111) does *not* obey normal energy scaling.

From Fig. 12, parallel translational energy is seen to inhibit dissociation for low E_Z and promote dissociation for high E_Z . Between $E_Z=0.17$ eV and $E_Z=0.22$ eV, the dissociation curves are seen to cross. This particular effect of parallel translational energy on dissociation was previously seen in calculations employing a model PES with only energetic corrugation^{44,65} and no geometric corrugation. In those model calculations, the dissociation curves crossed in a single point. This suggests that, although the 3D PES used in the present calculations is both energetically and geometrically corrugated, the energetic corrugation predominates.

In Figs. 13(a)–13(d), diffraction probabilities are given as function of the incident translational energy, E_Z . The diffraction probability plotted is the sum of the probability to scatter into diffraction states n and $-n$, n being the diffraction quantum number. Each probability curve is labeled with $p=|n|$, the diffraction order. Results are shown for $\vartheta_i=0^\circ, 30^\circ, 45^\circ$, and 60° . Although considerable diffraction is found for ϑ_i up to 45° , the general trend found is a decrease in the probability to scatter into higher diffraction order with increasing parallel translational energy. This phenomenon is expected to be quite general and not restricted to the H₂/Pt(111) system in particular, although it may vary in strength from one system to the other. The effect can be explained in two ways. First, consider the potential as function of Z and X for $r=r_e$, r_e being the molecule's gas phase equilibrium bond length ($r_e=1.41 a_0$) (see Fig. 14). At the collision energies considered in this study, the molecule will be able to come much closer to the surface at $X=(1/2)L$ than at $X=0$. However, the indented region visible in Fig. 14 for $X=(1/2)L$ will be much less accessible for large incidence angles, ϑ_i , leading to a lower effective corrugation for high

FIG. 13. The 3D diffraction probability for diffraction orders $p=0-3$ as a function of the normal incident translational energy, E_Z , is shown for different values of ϑ_i (K_X^0). Indicated along the top horizontal axis of each plot is the incidence angle θ_i corresponding to E_Z and K_X^0 (for $\vartheta_i=K_X^0=0$, $\theta_i=0$ for all E_Z).

θ_i . This should reduce the probability of diffraction. Second, the energy difference between the specular channel and higher order diffraction channels will generally increase with increasing K_X^0 , which will lead to a decrease of the higher order diffraction probabilities if these are inversely proportional to the energy transferred, as is usually the case in scattering.⁶⁶

The substantial diffraction found in the present calculation is in contradiction with experiment. However, in the present 3D calculations the lattice constant (which followed from our choice of the X-axis) used was quite large ($L=9.07$ bohr), resulting in a fairly small spacing in momentum space ($\Delta K_X=2\pi/L$). For such a small value of ΔK

FIG. 14. A contour plot of the potential (V^{III}) relative to the gas phase minimum ($V_0=-4.794$ eV) as function of Z and X is shown for $r=1.41$ bohr. The values given with the contours are in eV.

FIG. 15. A comparison of the experimental data of Luntz *et al.* (Ref. 18) and the present calculations is shown. Curves of the same angle ϑ_i are to be compared. The ϑ_i shown ($\vartheta_i=0^\circ$, 30° , and 45°) correspond to $K_X^0=0$, 4.31, and 7.46 a.u., respectively. The dissociation probabilities are shown as function of the total incident energy, E_i .

diffraction can occur with little energy transfer, thereby making diffraction efficient in the present 3D model. Including motion along Y also, the unit cell (see Fig. 2) can be described within an oblique coordinate system having a lattice constant $L'=L/\sqrt{3}$. This smaller lattice constant leads to a larger quantum of diffraction, and therefore diffraction probabilities are likely to be smaller in a 4D model also including motion in Y .

A quantitative comparison between the experimental results of Luntz *et al.*¹⁸ and our calculated 3D reaction probabilities was also made. Even though the comparison is made for reduced (3D) dimensional calculations, such a comparison can still be meaningful. In the experiment the reaction probability was measured as function of the total translational incident energy for a fixed angle of incidence θ_i . The present calculations were done for fixed K_X^0 as explained earlier. To make a comparison possible, from the experimental data the reaction probability curves as function of the total incident translational energy for fixed K_X^0 , instead of fixed θ_i , were obtained. This was done in the following way. For each experimental curve depicting the dissociation probability as function of the total incident translational energy, E_i , for a fixed incidence angle, θ_i , the particular E_i can be computed that satisfies $E_X^0=E_i \sin^2 \theta_i$, where E_X^0 is the initial energy parallel to the surface used in the calculation. For this particular value of E_i the dissociation probability is then determined by reading off the interpolated experimental data (see Fig. 1 of Ref. 18). This was repeated for all θ_i for which experimental data is available, and for all energies E_X^0 for which calculation have been done. The results for $K_X^0=0$, 4.31, and 7.46 a.u. ($\vartheta_i=0^\circ$, 30° , and 45°) are shown in Fig. 15. Note that the experimental results were for D_2 dissociating on Pt(111), whereas the present calculations are for H_2 on Pt(111), but this should not hamper the comparison: as pointed out before the isotope effect was small in the calculations, while no isotope effect was detected in the experiments¹⁸ for normal incidence. Assuming the isotope

effect to be small also for off-normal incidence, a comparison is justified.

Comparing curves of the same $K_X^0(\vartheta_i)$ for theory and experiment in Fig. 15, we find at higher energies experiment and theory do not agree well. However, the 3D results are already in quite good quantitative agreement with experiment for the onset of the reaction probabilities, and the dependence of the onset on $K_X^0(\vartheta_i)$. The overall agreement with experiment is expected to improve with increasing dimensionality of the calculations, as we hope to demonstrate in future research.

Finally, an important issue concerning reaction of H_2 on Pt(111) is to what extent defects and steps affect the reaction, also under thermal conditions. Because we have only performed calculations on scattering from the perfect (111) face, we cannot say much about this issue. Our findings that reaction on the perfect (111) surface is efficient at low collision energies under normal incidence, but much less efficient at low collision energies and large incidence angles, does not conflict with the conclusions of Luntz *et al.*¹⁸ on the influence of steps and defects on reaction. From their experiments, they found that steps have only a small effect on the measured dissociation probability at energies larger than 70 meV, under normal incidence. They also noted that this does not rule out an important role for steps and defects at large incidence angles, or at even lower collision energies. It should be pointed out that such incidence conditions can be quite relevant in catalysis, and that Verheij, Poelsema, Comsa, and co-workers found that defects and steps can have a fairly large effect on H_2 background gas adsorption at $T=300$ K.⁸ The issue of the influence of steps and defects on reaction of H_2 on Pt(111) certainly deserves more attention in the future.

IV. CONCLUSIONS

Two-dimensional (2D) and three-dimensional (3D) quantum dynamics calculations have been performed on dissociative and diffractive scattering of H_2 from Pt(111), using the time-dependent wave packet method. The main motivation for this research is a paradox about the degree of corrugation of the H_2 /Pt(111) system that arose from molecular beam experiments. Much of the latter have been performed to resolve conflicting views on the dissociation of H_2 over a Pt surface, a process of great importance in connection with the role of Pt as a hydrogenation catalyst.

In both the 2D and 3D calculations, the H_2 molecular bond was kept parallel to the surface and dissociation takes place perpendicular to the X -axis defined in Fig. 2. In the 3D calculations, the molecule's degrees of freedom are (1) motion normal to the surface, (2) vibrational motion, and (3) motion along the X -axis. In the 2D calculations, the molecule is constrained to move above a fixed value of X .

The dynamics calculations used a potential energy surface that was obtained using density functional theory, employing a generalized gradient approximation and a slab representation of the surface.

Results of 2D calculations for initial $v=0$ H_2 showed a large variation in the dynamical barrier height, E_0 , with the

impact site X. Furthermore, for each site investigated, E_0 is substantially smaller than the barrier height in the PES, E_b . Also a small isotope effect was found; for higher initial energies $\nu=0$ D₂ is shifted to higher energies by about 0.02 eV. Calculations for initial $\nu=1$ H₂ showed a large vibrational enhancement of reaction. These findings are rather surprising, since all the barriers are located in the entrance channel, excluding the possibility of a reduced mass effect by which vibrational energy can be released. Upon inspection of the potential along the H–H distance in the entrance channel, we found that the force constant associated with the vibration decreases towards the barrier. As a consequence, the vibrational energy becomes smaller as the molecule approaches the barrier, even though there is little or no change in the reduced mass associated with the vibration perpendicular to the reaction path. The vibrational energy released can flow to motion along the reaction path, explaining why E_0 is substantially smaller than E_b for initial $\nu=0$ H₂. For initial $\nu=1$ H₂ even more vibrational energy is released, resulting in a large vibrational enhancement of reaction. For initial $\nu=0$ D₂, the amount of vibrational energy release is less than for $\nu=0$ H₂ because D₂ has a smaller vibrational frequency associated with its vibrational ground state.

The present findings for H₂+Pt(111), and previous computational results for H₂+Pd(100),⁴¹ make one critical about the standard association of vibrational enhancement with a late barrier. Other specific features of the PES might also contribute significantly to a vibrational enhancement effect.

Three-dimensional calculations were done for $\nu=0,1$ H₂ and $\nu=0$ D₂, for normal incidence and off-normal incidence. For normal incidence a small isotope effect is found (0.017 eV), and a large vibrational enhancement of reaction. Both effects can be understood from a decrease of the force constant associated with the H₂ vibration, as was already discussed for the 2D calculations. In seeded molecular beam experiments by Luntz *et al.*,¹⁸ no isotope effect was found, and also no vibrational enhancement of reaction was found. However, the size of the isotope effect found in the present calculations might be too small to be observable in the experiment. Furthermore, an analysis performed here suggests that seeded beam experiments do not represent an appropriate tool for determining whether a reaction is vibrationally enhanced if the reaction of the $\nu=0$ molecule does not show an energetic threshold.

Calculations for off-normal incidence were done only for $\nu=0$ H₂. The dissociation probabilities show a clear dependence on the energy in motion parallel to the surface, the dependence being that motion parallel to the surface inhibits dissociation at low collision energies. Therefore, dissociation of H₂ on Pt(111) does *not* obey normal energy scaling in the present 3D model. These results are in agreement with molecular beam experiments.

Diffraction was also studied. The results of 3D calculations for various angles of incidence showed that the probability of diffraction decreases for increasing angle of incidence. Nevertheless, the amount of diffraction found is still quite large, whereas experiment¹³ found only very little diffraction. The discrepancy with experiments could be due to the choice of the X-direction in the 3D model; with the

choice made, the surface lattice constant ($L=9.07$ bohr) was somewhat larger than the actual value ($L=5.24$ bohr).

Finally, a comparison of the present 3D calculations and experimental results obtained by Luntz *et al.*¹⁸ was made. A good quantitative agreement on the onset of the dissociation was found for various angles of incidence. For energies higher than the onset energy the results do not agree well, but the agreement is expected to improve with increasing dimensionality of the dynamics calculations.

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