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published in
Journal of Chemical Physics
2003

DOI (link to publisher)
10.1063/1.1540981

document version
Publisher's PDF, also known as Version of record

citation for published version (APA)
Kingma, S. M., Somers, M. F., Pijper, E., Kroes, G., Olsen, R. A., & Baerends, E. J. (2003). Diffractive and reactive scattering of (v=0, j=0) HD from Pt(111): Six-dimensional quantum dynamics compared with experiment. *Journal of Chemical Physics*, *118*(9), 4190-4197. https://doi.org/10.1063/1.1540981

JOURNAL OF CHEMICAL PHYSICS VOLUME 118, NUMBER 9 1 MARCH 2003

Diffractive and reactive scattering of $(v=0,\ j=0)$ HD from Pt(111): Six-dimensional quantum dynamics compared with experiment

Sikke M. Kingma, Mark F. Somers, Ernst Pijper, and Geert-Jan Kroes
Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Roar A. Olsen and Evert-Jan Baerends
Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(Received 21 October 2002; accepted 5 December 2002)

We present results of $(v=0,\ j=0)$ HD reacting on and scattering from Pt(111) at off-normal angles of incidence, treating all six molecular degrees of freedom quantum mechanically. The six-dimensional potential energy surface (PES) used was obtained from density functional theory, using the generalized gradient approximation and a slab representation of the metal surface. Diffraction and rotational excitation probabilities are compared with experiment for two incidence directions, at normal incidence energies between 0.05–0.16 eV and at a parallel translational energy of 55.5 meV. The computed ratio of specular reflection to nonspecular in-plane diffraction for HD+Pt(111) is lower than found experimentally, and lower for HD+Pt(111) than for H_2 +Pt(111) for both incidence directions studied. The calculations also show that out-of-plane diffraction is much more efficient than in-plane diffraction, underlining that results from experiments that solely attempt to measure in-plane diffraction are not sufficient to show the absence of surface corrugation. Discrepancies in rotational excitation and diffraction probabilities between theory and experiment are discussed, as well as possible future improvements in the dynamical model and in the calculation of the PES. *© 2003 American Institute of Physics.* [DOI: 10.1063/1.1540981]

I. INTRODUCTION

Since the early 1980s, the reactive, the rotationally elastic and inelastic, and the diffractive scattering of molecular hydrogen from metal surfaces have been studied extensively, both experimentally[1–17] and theoretically.[17–28] Much attention has been devoted to HD scattering from Pt(111) because of, *inter alia*, the high probabilities for rotational excitation to only a limited number of accessible rotational states. Experimental efforts by Cowin and co-workers[1,2] have been followed by several theoretical studies of this system, employing either Wigner R-matrix theory[27,29] or Engdahl–Moiseyev–Maniv T-matrix methods[28] to obtain rotationally inelastic scattering probabilities. In all of these calculations, it was assumed that the system could be treated accurately by neglecting vibration and dissociative chemisorption and conserving the magnetic rotational quantum number, m_j, of incident HD. Furthermore, diffraction, and thus translation in X and Y, was neglected, leading to a two-dimensional Hamiltonian depending only on the molecule–surface distance Z and the polar angle of orientation θ (the angle between the molecular axis and the surface normal). The potential energy surface (PES) in these studies was approximated by a Morse potential that was adapted to allow for anisotropy in θ. These approximations were considered justified, because Pt(111) was thought to be a noncorrugated (“flat”) surface, as was suggested by Cowin *et al.* on the basis of their molecular beam experiments in which no significant (in-plane) diffraction was observed.[2] The main aim of these theoretical calculations was to reproduce the bound level resonances of the HD+Pt(111) physisorption interaction potential that were encountered by Cowin *et al.*[1]

The reaction of H_2 on Pt(111) has likewise received attention. In 1990, Luntz *et al.*[12] concluded from their molecular beam study of dissociative chemisorption of H_2 and D_2 on Pt(111) that the PES must be rather corrugated, since the reaction probability was found to depend on the initial parallel momentum, instead of scaling with normal translational energy. The latter finding and the observation of little diffraction in the experiments of Cowin *et al.*[2] represent a paradox:[30] The experiments on reaction suggest a corrugated surface, whereas the experiments on diffraction suggest a flat surface.

This controversy has been addressed in several theoretical studies[31–33] on H_2 scattering from Pt(111). In a study treating all six molecular degrees of freedom quantum mechanically[33] and employing a PES based on density functional theory (DFT),[34,35] it was found that reaction does not obey normal energy scaling, and that the diffraction is substantial, supporting the conclusion of Luntz *et al.*[12] It was suggested that the experiments by Cowin *et al.*[1,2] failed to find proof of the corrugation of the surface because they measured only in-plane diffraction and did not consider diffraction out of the plane of incidence (the out-of-plane diffraction was predicted to be substantial by the theory). Nevertheless, the calculations yielded more in-plane diffraction (relative to nondiffractive reflection) than Cowin's experiment. It was suggested that this difference might be due to a difference between HD and H_2; rotational excitation is ex-

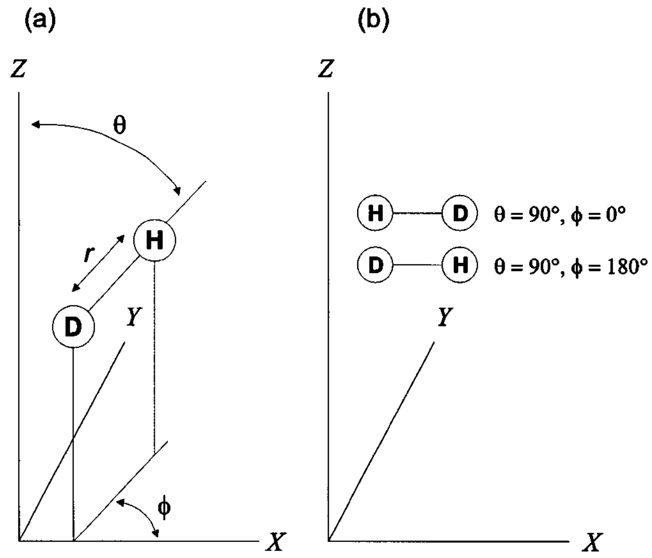

FIG. 1. The coordinate system used in this study. In (a) the HD center-of-mass coordinates (*X*, *Y*, and *Z*), the HD bond distance *r*, and the two orientational angles θ and ϕ are indicated. In (a) and (b), the conventions adopted for θ and ϕ are illustrated.

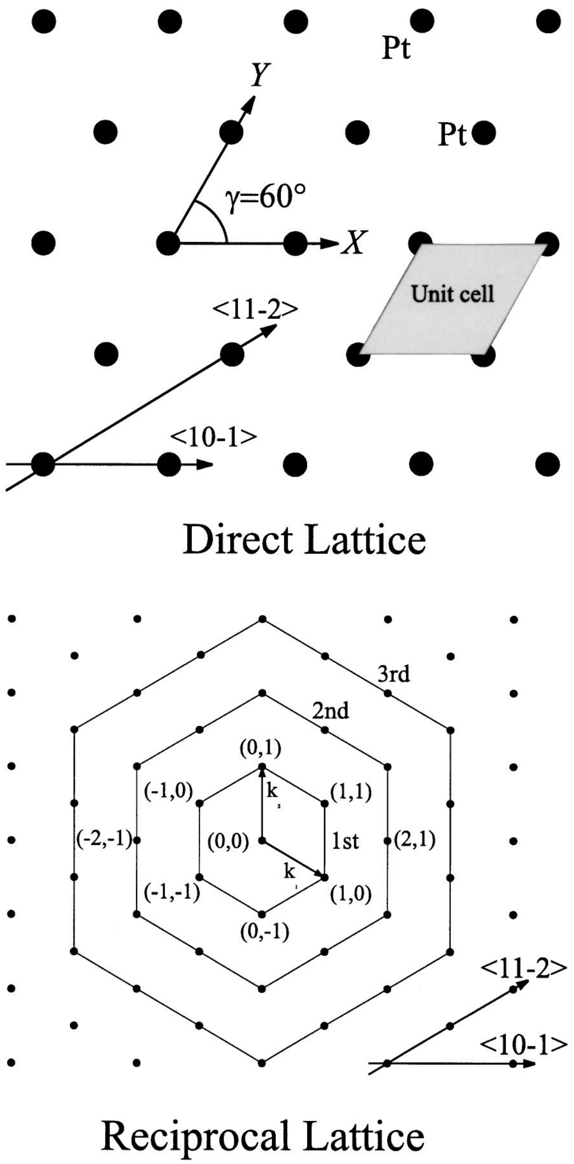

FIG. 2. The direct lattice (top) and reciprocal lattice (bottom) of the Pt(111) surface. The direct lattice shows the unit cell (shaded area) and the *X* and *Y* coordinate axes used. The skewing angle γ equals 60°. Points on the reciprocal lattice correspond to diffraction states allowed during scattering. The hexagonal rings define the diffraction order. In both figures, the ⟨101⟩ and ⟨112⟩ directions are indicated.

pected to be more efficient for HD than for H_2, and therefore increased competition of rotational excitation with diffraction might lead to lower diffraction probabilities for HD.

Our work addresses this question by comparing six-dimensional quantum dynamics results with experiment, thus offering the first results of dynamics calculations on a *heteronuclear* diatomic molecule scattering from a surface in which all molecular degrees of freedom are treated quantum mechanically. The dynamics method and the PES used are discussed in Secs. II A and II B, respectively. In Secs. III A–III C, reaction, rotational excitation, and diffraction results are discussed and, where possible, compared with experiment. Section IV offers a summary of our findings.

II. METHOD

A. Dynamics

In the quantum dynamics calculations, the Born–Oppenheimer approximation was used and it was assumed that the reaction takes place on the ground state PES only, thereby neglecting electron–hole pair excitations. The surface Pt atoms were frozen to their equilibrium positions, thereby neglecting the possibility of energy transfer involving phonons. For a discussion of these approximations, and a review of quantum dynamics methods for molecule–surface reactions, see Refs. 36–38.

The motion in the remaining six degrees of freedom (those of HD) was treated essentially without approximations. The coordinate system and the surface unit cell are shown in Figs. 1 and 2. The translational coordinates *X*, *Y*, and *Z* are the coordinates of the center-of-mass of the molecule. A system of skewed coordinate axes *X* and *Y*, with a skewing angle of 60°, was used to describe motion parallel to the surface. The coordinate *Z* describes the distance to the surface. The internal coordinates *r*, θ, and ϕ represent the H–D distance and the polar and the azimuthal angles of orientation of the HD axis.

The calculations were performed using the same implementation of the time-dependent wave packet (TDWP) method[39] as used before to study $H_2+\mathrm{Pt}(111)$.[33] We employed the split-operator formalism[40] in which the propagator is symmetrically split into two kinetic energy parts and one potential energy part. The wave function was represented by an expansion in a finite nondirect product basis set (FBR) of spherical harmonics $Y_{jm_j}(\theta,\phi)$ with expansion coefficients $c_{jm_j}(X,Y,Z,r)$, where *X*, *Y*, *Z*, and *r* are points on Fourier grids with constant spacings ΔX, ΔY, ΔZ, and Δr.

The action of the translational and vibrational kinetic energy operator part of the propagator on the wave function, $c_{jm_j}(X,Y,Z,r)$, was implemented using Fast Fourier

TABLE I. Input parameters of the wave packet calculations for HD scattering from Pt(111).

Parameter	Description	Value
$E_{\parallel}$	Parallel incidence energy (eV)	0.055 5
	Normal incidence energy range (eV)	0.05–0.16
Z_0	Location of center of wave packet on Z grid (a_0)	11.0
$Z_{\min}$	Starting value of Z grid (a_0)	-1.0
N_Z	Number of grid points in Z	90
ΔZ	Grid spacing in Z (a_0)	0.15
N_r	Number of grid points in r	40
Δr	Grid spacing in r (a_0)	0.20
$r_{\min}$	Starting value of r grid (a_0)	0.40
N_X	Number of grid points in X	16
N_Y	Number of grid points in Y	16
a	Surface lattice constant (a_0)	5.239 66
$j_{\max}$	Maximum value of j in rotational FBR	16
N_{tot}[a]	Size scattering basis set	266 million
Δt	Size of time step in propagation (atomic units)	2.5
$T_{\max}$	Total propagation time (atomic units)	35 000

[a] N_{tot} is the number of rotational channels in the FBR multiplied by $N_Z N_r N_X N_Y$.

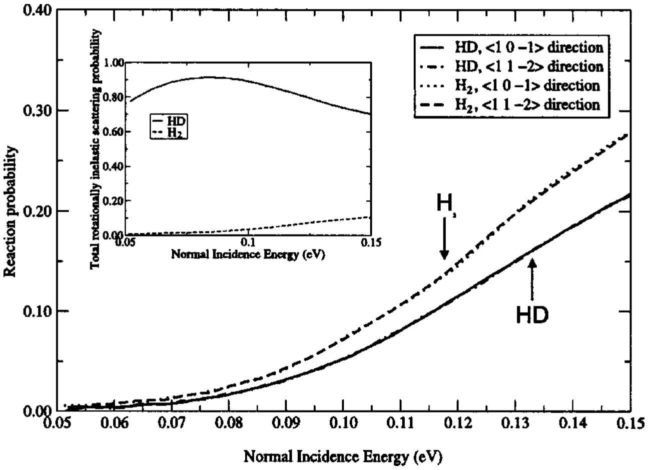

FIG. 3. Dissociative chemisorption probabilities for ($v=0$, $j=0$) HD (present work) and H_2 (Ref. 33) as a function of normal incidence energy, for an initial parallel translational energy of 55.5 meV. Results for both the $\langle 101\rangle$ and $\langle 112\rangle$ incidence directions are shown. The inset shows the total rotationally inelastic scattering probabilities P($v=0$, $j=0\rightarrow v'=0$, $j'\neq 0$) for H_2 and HD for the $\langle 112\rangle$ incidence direction at a parallel translational energy of 55.5 meV, as a function of normal incidence energy.

transforms[41] in X, Y, Z, and r. For the rotational energy operator, no transforms were necessary, since the spherical harmonics are eigenfunctions of this operator.

In evaluating the action of the potential energy operator part of the propagator on the wave function, a Gauss-associated-Legendre method developed by Corey and Lemoine[42,43] was used to transform the $c_{jm_j}(X,Y,Z,r)$ from the FBR in j and m_j to a discrete variable representation (DVR) in θ and ϕ, and back to the FBR (after multiplication with the potential energy).

The scattering amplitude formalism[44,45] was used to compute state-to-state scattering probabilities for the range of initial translational energies in Z contained in the wave packet (0.05–0.16 eV). Reaction probabilities were calculated by subtracting the summed scattering probabilities from unity. We performed calculations for ($v=0$, $j=0$) HD incident along the $\langle 101\rangle$ and $\langle 112\rangle$ directions (Fig. 2) with an initial translational energy parallel to the surface of 55.5 meV. This corresponds to an incidence angle of 45° with the surface normal at an initial translational energy in Z of 55.5 meV, thus exactly reproducing the conditions of one of the experiments of Cowin *et al.*[2] for this incidence energy.

The most relevant parameters used in the calculations are listed in Table I.

B. PES

The six-dimensional PES used in these calculations was originally developed for the $H_2+\mathrm{Pt}(111)$ system, using the program BAND (Ref. 46) for performing density functional theory (DFT) calculations for $\mathrm{H}+\mathrm{Pt}(111)$ and $H_2+\mathrm{Pt}(111)$ systems, employing the generalized gradient approximation (GGA).[47,48] Relativistic effects, which are important for Pt, are taken into account by the zeroth-order regular approximation (ZORA).[49] The "corrugation reduction" scheme by Salin and co-workers[35] was used to construct the $H_2+\mathrm{Pt}(111)$ PES from a number of two-dimensional PESs. More information on the construction of this PES has been published in Refs. 34 and 50.

Within the Born–Oppenheimer approximation, a PES developed for H_2 is equally fit for calculations on an isotopomer, *in casu* HD. The symmetry with respect to the center-of-mass which exists in H_2, however, is absent in HD. This is because in HD, the center-of-mass is closer to the D atom than to the H atom. The potential energy for an HD molecule with center-of-mass coordinates (X,Y,Z,r,θ,ϕ) is equal to the potential energy of an H_2 molecule with coordinates (X',Y',Z',r,θ,ϕ), where X', Y', and Z' are given by

$$X'=X+\frac{r}{2}\left[\frac{\sin(\gamma-\phi)}{\sin\gamma}\sin\theta\right]\left[\frac{m_{\mathrm{D}}-m_{\mathrm{H}}}{m_{\mathrm{D}}+m_{\mathrm{H}}}\right], \tag{1a}$$

$$Y'=Y+\frac{r}{2}\left[\frac{\sin\phi}{\sin\gamma}\sin\theta\right]\left[\frac{m_{\mathrm{D}}-m_{\mathrm{H}}}{m_{\mathrm{D}}+m_{\mathrm{H}}}\right], \tag{1b}$$

$$Z'=Z+\frac{r}{2}\cos\theta\left[\frac{m_{\mathrm{D}}-m_{\mathrm{H}}}{m_{\mathrm{D}}+m_{\mathrm{H}}}\right]. \tag{1c}$$

In these equations, m_{D} and m_{H} represent the masses of D and H, respectively, and γ is the skewing angle ($0°<\gamma\leqslant 90°$): 60° in the case of the Pt(111) surface. Extra conventions have to be adopted for θ and ϕ: rotations of 180° over θ no longer leave the molecule–surface interaction invariant and the same applies to rotations of 180° over ϕ for an orientation of the molecule parallel to the surface. The conventions adopted are implied by the expressions above and shown in Fig. 1.

III. RESULTS AND DISCUSSION

A. Reaction

In Fig. 3, the dissociative chemisorption probabilities of HD and H_2 (Ref. 33) are plotted as a function of normal incidence energy, for a parallel translational energy of 55.5

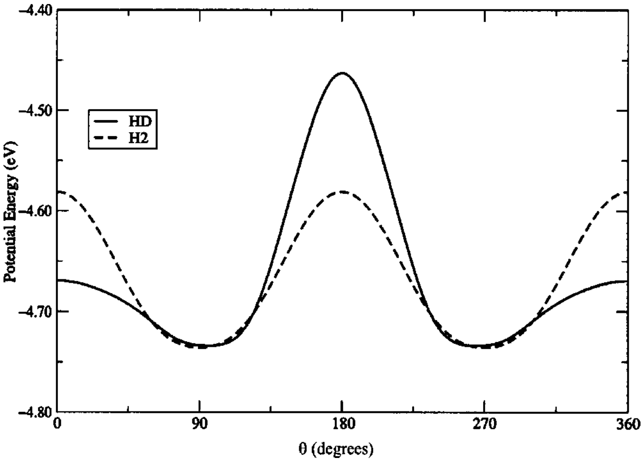

FIG. 4. Plot of the potential energy as a function of θ for HD and H_2 at the top site ($X=Y=0.0$). The center-of-mass of the molecule is fixed at the H_2 barrier location ($r=1.46\,a_0$, $Z=4.25\,a_0$) with $\phi=120°$. The difference between the highest and lowest values of the potential energy when rotating over θ is greater for HD (0.27 eV) than for H_2 (0.15 eV).

meV, and for incidence along the $\langle 10\bar{1}\rangle$ and $\langle 11\bar{2}\rangle$ directions. No significant dependence of reaction on the incidence direction was found for either isotopomer. Over the entire energy range, H_2 dissociation is more efficient than HD dissociation. This difference is most probably due to greater competition between reaction and rotational excitation in HD. As the inset to Fig. 3 shows, the total probability for rotational excitation is much larger for HD than for H_2. One reason that rotational excitation is so efficient for HD is that HD is a heteronuclear molecule, the $j=1$ and $j=3$ states being accessible from the rotational ground state; many molecules return to the gas phase in these states (see below), which are not accessible to (homonuclear) $j=0$ H_2. The energy transferred to rotation is subsequently no longer available for traversing the barrier to dissociation. Furthermore, because the center-of-mass of HD is not situated halfway between the nuclei, orientations that differ in the polar angle by 180° are not equivalent, and therefore, the potential for HD is more anisotropic than for H_2 (Fig. 4), which is expected to result in more rotational excitation and less reaction. Finally, the energy spacing between the rotational levels of HD is smaller than in H_2, thereby again enhancing rotational excitation and inhibiting reaction.

Cowin *et al.* did not measure reaction (sticking) probabilities for HD+Pt(111). In an attempt to account for lost flux, they did, however, remark that reaction could play a significant role in the attenuation of their signal. Since the reaction probability at the energy considered has been shown to be relatively small in both theoretical calculations[33] and experiments on H_2 and D_2 on Pt(111),[12,13] it is more likely that the greater part of the loss of flux in Cowin's experiment should be attributed to other causes, such as out-of-plane diffraction (see Sec. III C).

B. Rotational excitation

In Fig. 5, rotationally elastic and inelastic excitation probabilities $P(v=0, j=0 \rightarrow v'=0, j=j')$ are presented as a function of initial normal incidence energy, for $j'=0-3$ and for an initial parallel energy of 55.5 meV along the $\langle 11\bar{2}\rangle$ direction. At an incidence angle of 45° (i.e., at an initial translational energy in Z of 55.5 meV), the excitation probabilities are 0.68 and 0.11 for the $j=0\rightarrow j=1$ and $j=0\rightarrow j=2$ transitions, respectively. As already explained in Sec. III A, rotational excitation of HD is expected to be more efficient than that of H_2 because HD is asymmetric and has more closely spaced energy levels. An additional explanation for these large rotational excitation probabilities at low collision energies has been suggested in previous theoretical[17,33,51] and experimental[7,17] studies. Because the threshold energy to reaction is equally low, molecules are able to approach the barrier closely at these low energies, where they experience a high anisotropy of the potential energy, allowing efficient rotational excitation.

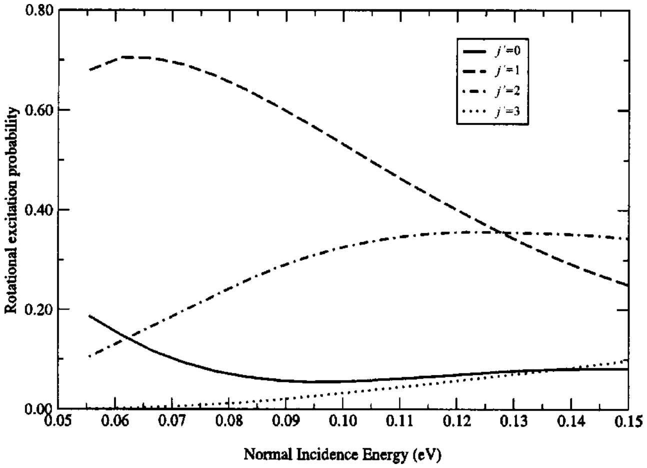

FIG. 5. Absolute rotational excitation probabilities for ($v=0$, $j=0$) HD scattering from Pt(111) as a function of normal incidence energy, for incidence along the $\langle 112\rangle$ direction. The initial parallel translational energy is 55.5 meV, reproducing the experimental conditions of Cowin's experiment (Ref. 2) for 55.5 meV translational energy in Z (i.e., at an incidence angle of 45°). The probabilities have been summed over all diffraction states and m_j channels. Incidence along the $\langle 101\rangle$ direction yields virtually the same results, which are not shown in the plot.

Cowin *et al.* found virtually identical rotational excitation probabilities for the two incidence directions at this energy (cf. Fig. 4 of Ref. 2). They considered this result an illustration of the weak corrugation of the surface.[1,2] Our computed results are also practically identical for the $\langle 101\rangle$ and $\langle 112\rangle$ directions. We believe, however, that this result can be understood from somewhat different arguments, which are similar to those used in Refs. 33 and 30. Because the parallel momentum of the molecules is small (i.e., it is not greater than the initial momentum normal to the surface), the molecules will be scattered by the first barrier they encounter, instead of experiencing the full range of the variation of the anisotropy in the plane of incidence. The calculations of Ref. 33 have shown that for greater parallel momentum (i.e., greater than the initial momentum normal to the surface), rotational excitation probabilities start to differ significantly for the two incidence directions: rotational excitation for incidence along the $\langle 101\rangle$ direction roughly obeys normal energy scaling, whereas for incidence along the more corrugated $\langle 112\rangle$ direction, rotational excitation is

TABLE II. Rotational excitation probabilities for ($\mathbf{G}=0$) scattering of ($v=0$, $j=0$) HD from Pt(111), for incidence along the $\langle 101\rangle$ direction at a normal incidence energy of 55.5 meV and equal parallel translational energy. The probabilities have been normalized to unity.

	$j=0\rightarrow j=0$	$j=0\rightarrow j=1$	$j=0\rightarrow j=2$
Cowin *et al.*[a]	0.03	0.40	0.57
This work	0.16	0.72	0.12

[a] Reference 2.

coupled more strongly to parallel motion. The incidence direction-independent results for HD+Pt(111) obtained by Cowin *et al.*[2] and by us for a low parallel energy are therefore only typical for initial parallel energies less than or equal to the initial energy normal to the surface.

A quantitative comparison of the results of our calculations with the experimental results can only be performed for a normal incidence energy of 55.5 meV; together with an equal amount of parallel translational energy, the total energy of 111 meV of Cowin's beam is then reproduced. Because the experiments were performed for various incidence angles and fixed total translational energy,[2] whereas our calculations were performed for fixed parallel energy and a range of normal translational energies, a comparison over the entire energy range is not possible without performing additional, costly calculations.

Although our results agree qualitatively with the results of Cowin *et al.*[2] in that we also found identical rotational excitation probabilities for the two incidence directions, our results do not agree quantitatively with their results. In Table II, the rotational excitation probabilities calculated in our study are compared with the *relative* excitation probabilities of Cowin *et al.* To make this comparison meaningful, our probabilities have been normalized to unity to yield *relative* numbers as well. Furthermore, the experimental rotational excitation probabilities represent probabilities for phonon-elastic, nondiffractive scattering ($\mathbf{G}=0$).[2] In particular, although the measurements were performed for a surface temperature $T_S=500\,\mathrm{K}$, a Debye–Waller attenuation model was used to extrapolate the results to a 0 K surface, in order to allow the data to be compared with theoretical calculations on a rigid surface.[2] In Table II, we therefore compare our rigid surface results for rotational excitation with $\mathbf{G}=0$ with the experimental rotational excitation probabilities.

In our calculations, the majority of the molecules scatter back to the gas phase in the $j=1$ state, whereas in Cowin's experiment, the $j=1$ and $j=2$ states are both highly populated. This discrepancy can be due to inaccuracies in the PES and in the dynamical model. Inaccuracies in the PES can be due to approximations inherent in DFT as well as to small errors that were made in the interpolation of the DFT data to obtain a global PES. With respect to the latter, we note that extensive tests have shown that the representation of the DFT data by the PES is accurate to within 30 meV in both the entrance and barrier regions of the PES.[34] The representation of the DFT data by the PES should therefore be much more accurate than for the H_2+Cu(100) case, for which Watts *et al.* recently published a comparison with experimental data for rotational excitation.[17] Although it cannot be ruled out that small errors resulting from the interpolation procedure affect the present results, we believe that the results are probably more affected by approximations now made in DFT. For instance, it is known that the GGA (Refs. 47, 48) used in the construction of the PES (Ref. 50) does not yield a correct description of the attractive van der Waals interaction between the molecule and the surface. This means that the van der Waals physisorption well, which has an estimated depth of 55 meV,[52] the estimation being based on rotationally mediated selective adsorption,[1,52] is absent from our PES. The incorrect description of the van der Waals energy could well result in errors in the location of the barriers in the PES, which in turn could lead to errors in the anisotropy of the PES in the region near the barrier, which is thought to be important for rotational excitation. For this reason, we believe that attempts to improve the PES to obtain a better description of rotational excitation of HD on Pt(111) should focus on correctly incorporating the van der Waals interaction in the DFT description of the PES. Over the past few years, density functionals for calculating van der Waals interaction energies have been developed,[53–57] and perhaps these or other yet to be developed methods can be used in future research to improve the accuracy of the PES.

We now turn to possible shortcomings in the dynamical model, such as the neglect of phonons and of electron–hole pair excitations. With respect to the former, we note that Cowin *et al.* did make an attempt to extrapolate their experimental results to 0 K in order to obtain phonon-elastic excitation probabilities, which could presumably be compared to theoretical results employing a rigid surface approximation. However, as they note themselves, the Debye–Waller model they applied for extrapolating their results to 0 K was developed for single molecule–surface bounces, and at their experimental normal collision energy (55 meV), many collisions are likely to suffer multiple Debye–Waller attenuation, due to trapping in the van der Waals physisorption well.[2] The increased importance of energy exchange with phonons under conditions where trapping may occur has been pointed out in a recent theoretical study of rotational excitation of H_2 on Pd(111).[58] Experiments on H_2+Pd(111) (Ref. 59) as well as on H_2+Cu(100) (Ref. 16) have shown that substantial amounts of energy may be exchanged with the surface in rotationally inelastic scattering. Because an improved description of the competition of phonon-inelastic scattering with phonon-elastic scattering should yield a better description of phonon-elastic scattering, we believe that incorporating phonons in the dynamical model would represent another important step towards an improved description of rotationally inelastic scattering of HD from Pt(111).

We do not believe that the neglect of electron–hole pair excitations represents a serious approximation. In recent experiments, Gergen *et al.*[60] found that the probability of exciting electron-hole pairs shows a power law dependence on the adsorption energy, low adsorption energies correlating with low excitation probabilities. In particular, they estimate an excitation probability of about 6% for an adsorption energy of about 0.2 eV, which is still larger than the estimated physisorption well depth for HD+Pt(111) of 55 meV. Probabilities for rotational excitation together with electron-hole pair

TABLE III. Ratio of specular reflection (**G**=0) to in-plane diffraction (**G**≠0) of HD scattering from Pt(111) at a normal incidence energy of 55.5 meV and equal parallel translational energy. In computing the ratios, diffraction probabilities have been summed over all rotational channels.

	System	$\langle 10\bar{1}\rangle$, in-plane $P(\mathbf{G}=0)/P(\mathbf{G}\neq 0)$	$\langle 11\bar{2}\rangle$, in-plane $P(\mathbf{G}=0)/P(\mathbf{G}\neq 0)$
Cowin *et al.*[a]	HD+Pt(111)	approx. 100	approx. 10
Reference 33	H_2+Pt(111)	20.0	4.71
This work	HD+Pt(111)	13.8	3.39

[a] Reference 2.

excitation would then be expected to be at the few percent level, so that the incorporation of electron-hole pair excitations in the dynamical model should not lead to important improvements in the description of rotationally inelastic scattering of HD from Pt(111).

A qualitative difference with experiment is that no resonances were found in the calculations. This is probably due to two causes. First, we did not perform calculations for the energies at which the resonances occur most strongly (<40 meV translational energy in Z). Quantum dynamics calculations on reaction of H_2 on Pd(100) (Ref. 22) and on reaction and rotational excitation of H_2 on Pd(111),[61] which used DFT PESs in a similar way to the present work, and which were performed for even lower energies, showed scattering resonances at these energies due to energy transfer to rotational and parallel motion, and the opening up of new scattering channels. Second, and more importantly, as previously mentioned, the generalized gradient approximation of DFT used in creating the 6D PES lacks a physically correct description of the attractive van der Waals interactions, which means that the van der Waals forces causing the resonances (through rotationally mediated selective adsorption in the physisorption well[1]) have not been incorporated in the PES.

C. Diffraction

In Table III, the computed ratios of specular to nonspecular in-plane diffraction of HD are compared with the experimental values of Cowin *et al.*,[2] and with the values computed for H_2+Pt(111) in Ref. 33. In this table, **G** denotes the momentum vector associated with diffraction: (**G**=0) corresponds to scattering without a change in parallel momentum and (**G**≠0) denotes diffractive scattering. Note that the ratios discussed here are for probabilities that represent sums over rotationally elastic and inelastic scattering.

As discussed in the Introduction, the authors of Ref. 33 suggested that the difference between experiment for HD +Pt(111) and theory for H_2+Pt(111) might be due to stronger competition between rotational excitation and diffraction in HD as compared with H_2, because of the expected higher rotational excitation probability of the former species. Our calculations show that this is not the case. For the conditions of Cowin's experiment, even smaller ratios were computed for HD (13.8 for incidence along the ⟨101⟩ direction and 3.39 for the ⟨112⟩ direction) than for H_2 (20.0 and 4.71, respectively). A possible explanation for the fact that we computed larger **G**≠0 probabilities for HD than for H_2 is that, since the mass of HD is greater than the mass of H_2, the energy gaps between HD diffraction channels are smaller, which is expected to lead to larger probabilities for diffractive scattering.

Above, the comparison between theoretical results for HD+Pt(111) and H_2+Pt(111) does not yet explain the discrepancies between the experimental and theoretical ratios (**G**=0 scattering)/(**G**≠0 in-plane scattering) for HD +Pt(111). We attribute these discrepancies to the same deficiencies of the PES and the model that are likely to cause the discrepancies between experimental and theoretical rotational excitation probabilities. The absence of a correct description of the attractive van der Waals interaction by the DFT functionals we used,[47,48] and the absence of an explicit description of energy exchange with surface phonons are most likely responsible for the present disagreement between theory and experiment for in-plane diffractive scattering of HD from Pt(111).

Cowin *et al.*[2] only measured in-plane scattering. As already mentioned, they found very little **G**≠0 in-plane scattering (1%–10% compared to specular reflection) and hence concluded that the surface must be rather flat. Furthermore, they estimated that the total **G**≠0 scattering would roughly equal three times the total **G**≠0 in-plane scattering.

For a parallel translational energy of 55.5 meV and both incidence directions considered, our calculations show that over the entire range of energies, out-of-plane scattering outcompetes in-plane scattering (*including* scattering with **G**=0) by a factor varying between approximately 1 and 6 [Fig. 6(a)]. The ratio of total out-of-plane to in-plane scattering is greater for the ⟨101⟩ than for the ⟨112⟩ direction. This is due to the nonavailability of first-order in-plane diffraction channels in the former direction, as discussed in Refs. 32, 33. The ratio of out-of-plane to **G**≠0 in-plane scattering [Fig. 6(b)] produces an even more impressive illustration of the importance of measuring out-of-plane scattering: For the ⟨101⟩ direction, more than 20 times as much out-of-plane diffraction is found in the calculations. Thus, out-of-plane scattering is much more important than suggested by the experimentalists,[2] who assumed that the total **G**≠0 scattering would roughly equal three times the **G**≠0 in-plane scattering, and were at a loss to explain the observed loss of flux in their experiments.[2] In particular, the extrapolation of the experimental results to $T_S=0$ K suggested that 28% of the molecules is scattered with **G**=0, and Cowin *et al.*[2] estimated that only 6% of the molecules should be diffracted. According to the present theoretical results, for the ⟨101⟩ incidence direction, 37% of the molecules is scattered with **G**=0 and 60% is diffracted, 58% of the scattering being due to out-of-plane scattering. Our results therefore strongly support the statement of Ref. 33 that conclusions about the corrugation of the surface should not be based on scattering experiments that only look at in-plane diffraction. Experimental techniques able to measure out-of-plane scattering are available[62–64] and it would be interesting to see whether the computed high out-of-plane diffraction probabilities are reproduced by such experiments.

IV. SUMMARY

We have presented results of 6D quantum dynamics calculations on the dissociative adsorption of HD on, and the

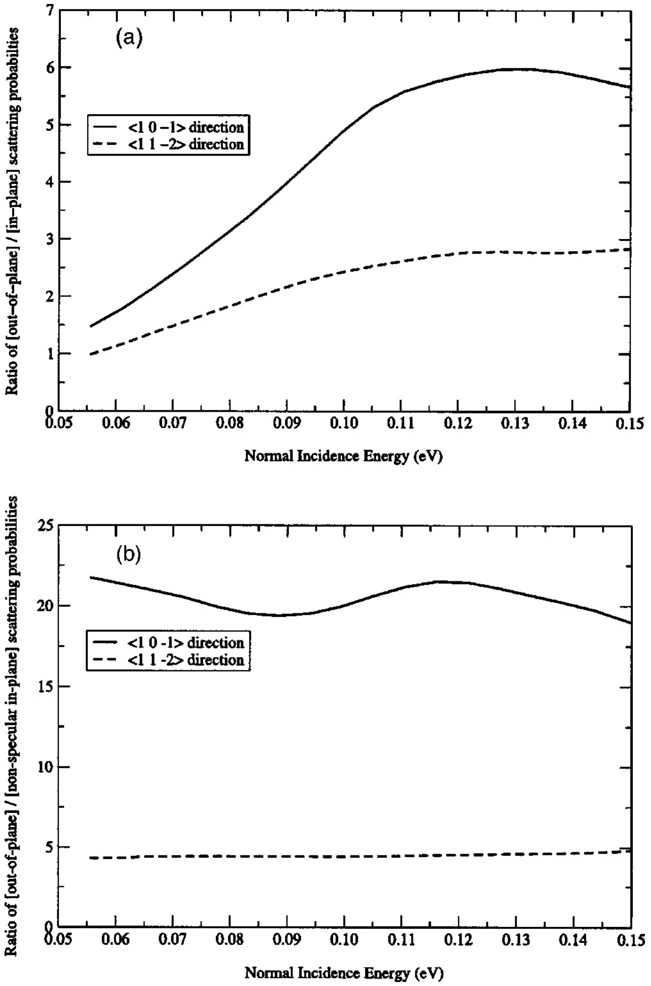

FIG. 6. Figure (a) shows a plot of the ratio of total out-of-plane to total in-plane (including $\mathbf{G}=0$ scattering) scattering probabilities of the HD $+$Pt(111) system for both the ⟨101⟩ and ⟨112⟩ incidence directions, as a function of normal incidence energy. Figure (b) shows the ratio of total out-of-plane to $\mathbf{G}\neq 0$ in-plane scattering probabilities. In both figures, the initial parallel translational energy is 55.5 meV.

rotationally inelastic and diffractive scattering of HD from Pt(111) at off-normal incidence (with a parallel translational energy of 55.5 meV) along the ⟨101⟩ and ⟨112⟩ surface directions, for a normal incidence energy range of 0.05–0.15 eV. The calculations were motivated by a discrepancy between experimental results for HD+Pt(111) (Ref. 2) and theoretical results for H_2+Pt(111),[33] the experiments for HD showing much less in-plane $\mathbf{G}\neq 0$ scattering relative to $\mathbf{G}=0$ scattering than the calculations for H_2. The main goal of the calculations was to determine whether the computed ratio of $\mathbf{G}=0$ to $\mathbf{G}\neq 0$ in-plane scattering would be higher for HD +Pt(111) than for H_2+Pt(111), explaining the above difference between theory and experiment. This was expected from the higher rotational excitation probabilities of HD, which could lead to more competition of rotational excitation with diffraction. The calculations showed, however, that for HD the ratio was lower rather than higher, i.e., that $\mathbf{G}\neq 0$ scattering is more probable, relative to specular scattering, than in H_2. We have suggested that this result could be explained by the lower energy gaps between diffraction channels in HD, which is caused by its greater mass.

The present calculations on HD+Pt(111) show a ratio of out-of-plane diffractive scattering to in-plane diffractive scattering that is much higher than assumed by the experimentalists.[2] Out-of-plane diffractive scattering may well account for much of the "lost flux" observed in their experiments.[2] Like previous studies,[31–33] the present calculations indicate that experiments only looking at in-plane diffraction are not well suited for probing the corrugation of the molecule–surface PES.

The reaction probability of HD is lower than that of H_2 over the energy range studied. This difference can be attributed to rotational excitation competing more strongly with reaction for HD than for H_2 reacting on Pt(111).

The computational results for rotational excitation of HD on and for in-plane diffractive scattering of HD from Pt(111) do not yet agree quantitatively with the experimental results. The deficiencies in the PES and in the dynamical model which are most likely responsible for the lack of agreement are the absence of a correct description of the attractive van der Waals interaction in the DFT-PES and the absence of an explicit description of energy exchange with phonons in the model. To improve the agreement between theory and experiment for scattering of HD from Pt(111), improvement of these two aspects should be the goal of future theoretical work.

ACKNOWLEDGMENTS

The dynamics calculations reported here have been carried out under a grant of computer time by the Dutch National Computing Facilities Foundation (NCF). The research of M.F.S. was supported by the Dutch National Research Council-Chemical Sciences (NWO-CW), through an "Open Competition grant." The research of R.A.O. was financed by NWO-CW and the National Research School Combination "Catalysis Controlled by Chemical Design" (NRSC-Catalysis). We are grateful to D. Lemoine for contributing the FBR-DVR scheme for rotational motion that has been implemented in our scattering code. We would like to thank H.F. Busnengo and A. Salin for their help in providing an accurate representation of the H_2+Pt(111) PES.

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