

Scattering of hydrogen molecules from a reactive surface: Strong off-specular and rotationally inelastic diffraction

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Six-dimensional quantum dynamical calculations of the scattering of H_2 from a Pd(100) surface using a potential energy surface derived from density-functional theory calculations are presented. Due to the corrugation and anisotropy of the PES strong off-specular and rotationally inelastic diffraction is found. The dependence of the diffraction intensities on the incident kinetic energy is closely examined. In particular we focus on the quantum oscillations for normal and off-normal incidence.

I. INTRODUCTION

Coherent elastic scattering of atoms or molecules from surfaces is a tool for probing surface structures and adsorbate–substrate interaction potentials. In particular helium atom scattering (HAS) has been used intensively to study surface crystallography and the shape of physisorption potentials (see, e.g., [1] and references therein). Hydrogen molecules have been utilized less frequently in order to study interaction potentials. The coherent elastic scattering of molecules is more complex than atom scattering because in addition to parallel momentum transfer the internal states of the molecule can be changed in scattering. This means in particular rotational transitions, because the energies typically employed in molecular scattering experiments are not sufficient to excite molecular vibrations.

Rotational transitions in elastic coherent scattering lead to the appearance of additional peaks in the diffraction pattern since the total kinetic energy of the molecule is changed. Most experimental studies of rotationally inelastic scattering of hydrogen have been performed at the surfaces of ionic solids [2,3]. (Here “inelastic” refers to energy exchange between the hydrogen degrees of freedom, not with respect to the substrate.) In the hitherto existing experiments of hydrogen scattering from metal surfaces the additional peaks could usually hardly be resolved [4–6] except in the case of HD scattering [6–8], where the displacement of the center of mass from the center of the charge distribution leads to a strong rotational anisotropy. Only recently Bertino *et al.* [9] clearly resolved rotationally inelastic peaks in the diffraction pattern of $D_2/Ni(110)$ in addition to rotationally elastic peaks, which had been observed before by Robota *et al.* [5]. Furthermore, Cvetko *et al.* [10] reported diffractive and rotationally inelastic scattering of $D_2/Rh(110)$.

In the case of hydrogen scattering from reactive surfaces, the repulsive interaction is not mediated by the tail of the metal electron density, but occurs rather close to the surface [11,12]. Due to the chemical nature of this interaction the potential is strongly corrugated and anisotropic with regard to the molecular orientation.

This requires a realistic microscopic description of the scattering dynamics. Existing theoretical studies of hydrogen scattering at surfaces have either treated non-reactive systems [13–17] or they were restricted to low dimensions on model potentials [18–20].

We have performed six-dimensional quantum dynamical calculations of the scattering of H_2 from Pd/(100) on a PES that was derived from density-functional theory calculations [11,21]. The PES exhibits a coexistence of activated with non-activated paths to adsorption together with a broad distribution of barrier heights. *All* six degrees of freedom of the hydrogen molecule are treated quantum dynamically in a coupled-channel scheme [22,23]. The substrate atoms are kept fixed. This is a serious approximation since it neglects phonon inelastic scattering. However, it is a reasonable to assume that rotation-diffraction transitions are relatively independent from phonon inelastic transitions [16]. Hence our rigid-surface results should be relevant for the fraction of coherently scattered molecules in experiments.

Our results show strong off-specular and rotationally inelastic diffraction which are caused by the corrugation and anisotropy of the PES. The intensities of the diffraction peaks exhibit a pronounced oscillatory structure as a function of the incident energy. We have already predicted such a structure for the sticking probability of $H_2/Pd(100)$ [21]. Very recently Rettner and Auerbach searched for these oscillations experimentally [24], but did not find any. We will carefully discuss the physical origin of the oscillations and point out why they might not have been detected. Hence this paper may also be regarded as an extended comment to Ref. [24].

II. COMPUTATIONAL DETAILS

The quantum dynamics is determined in a coupled-channel scheme within the concept of the *local reflection matrix* (LORE) [22]. This very stable method is closely related to the logarithmic derivative of the solution matrix and thus avoids exponentially increasing outgoing waves which could cause numerical instabilities.

In order to perform these demanding quantum dynamical calculations it is advantageous to utilize the symmetries of the scattering problem. The computational effort is much reduced if the incident parallel momentum corresponds to a reciprocal lattice vector (this includes the zero-vector for normal incidence). Therefore only calculations using such initial conditions are presented here.

The basis set used in the coupled-channel algorithm for the results presented here included rotational eigenfunctions with rotational quantum numbers up to $l_{max} = 8$, vibrational eigenfunctions with vibrational quantum numbers up to $v_{max} = 2$, and parallel momentum states with maximum parallel momentum $p_{max} = 7\hbar G$ with $G = 2\pi/a$, where a is the nearest neighbor distance between two Pd atoms. The convergence of the results with respect to the basis set has been checked carefully by calculations with maximum quantum numbers $l_{max} = 10$, $v_{max} = 3$, and $p_{max} = 10\hbar G$, respectively.

We use the same parametrization of the PES as in Ref. [21]. The results of Ref. [21] were in semi-quantitative agreement with experiment. In the meantime two predictions of the quantum dynamical calculations for $H_2/Pd(100)$, namely the strong rotational hindering of the dissociation at low kinetic energy [21,25] and the orientation dependence of adsorption and desorption [21], have been confirmed experimentally [26–28]. This shows that the PES of Ref. [21] gives a reliable description of the $H_2/Pd(100)$ interaction. For further computational details we refer to Ref. [29].

III. RESULTS AND DISCUSSION

One typical calculated angular distribution of H_2 molecules scattered at Pd(100) is shown in Fig. 1. The total initial kinetic energy is $E_i = 76$ meV. The incident parallel momentum corresponds to $2\hbar G$ along the $\langle 0\bar{1}1 \rangle$ direction. This leads to an incident angle of $\theta_i = 32^\circ$. The molecules are initially in the rotational ground state $j_i = 0$. (m, n) denotes the parallel momentum transfer $\Delta \mathbf{G}_{\parallel} = (mG, nG)$. The specular peak is the most pronounced one, but the first order diffraction peak (10) is only a factor of four smaller (note, that in a typical HAS experiment the off-specular peaks are about two orders of magnitude smaller than the specular peak). The results for the rotationally inelastic diffraction peaks $j = 0 \rightarrow 2$ have been summed over all final azimuthal quantum numbers m_j , as has been done for all results presented in the following. The excitation probability of the so-called cartwheel rotation with $m = 0$ is for all peaks approximately one order of magnitude larger than for the so-called helicopter rotation $m = j$, since the polar anisotropy of the PES is stronger than the azimuthal one.

This steric effect in scattering could already be expected from detailed balance arguments. According to

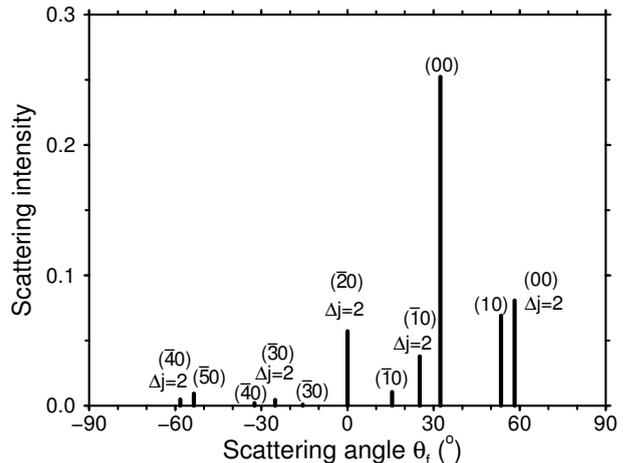


FIG. 1. Angular distribution of scattered H_2 molecules. The initial kinetic energy is $E_i = 76$ meV, the incident angle is $\theta_i = 32^\circ$ along the $\langle 0\bar{1}1 \rangle$ direction. The molecules are initially in the rotational ground state $j_i = 0$. The rotationally inelastic diffraction peaks have been marked with $\Delta j = 2$.

the principle of detailed balance, in a equilibrium situation the flux impinging on a surface from the gas-phase, which is rotationally isotropically distributed, should equal the desorption plus the scattering flux. Since in desorption the helicopter rotations are preferentially occupied [21,28], in scattering the cartwheel rotations have to be preferentially excited.

The intensity of the rotationally inelastic diffraction peaks in Fig. 1 is comparable to the rotationally elastic ones. Except for the specular peak they are even larger than the corresponding rotationally elastic diffraction peak with the same momentum transfer (m, n) . Note that due to the initial conditions the rotationally elastic and inelastic $(\bar{2}0)$ diffraction peaks fall upon each other.

The out-of-plane scattering intensities are not negligible, which is demonstrated in Fig. 2. The initial conditions are the same as in Fig. 1. The open circles correspond to rotationally elastic, the filled circles to rotationally inelastic diffraction. The radii of the circles are proportional to the logarithm of the scattering intensity. The sum of all out-of-plane scattering intensities is approximately equal to the sum of all in-plane scattering intensities. Interestingly, some diffraction peaks with a large parallel momentum transfer still show substantial intensities. This phenomenon is well known from helium atom scattering and has been discussed within the concept of so-called rainbow scattering [30].

A more detailed analysis of the diffraction intensities versus total incident kinetic energy is shown in Figs. 3-5. In Fig. 3 the intensities of four different diffraction peaks are plotted for normal incidence; Fig. 3a) shows rotationally elastic, Fig. 3b) rotationally inelastic diffraction. In

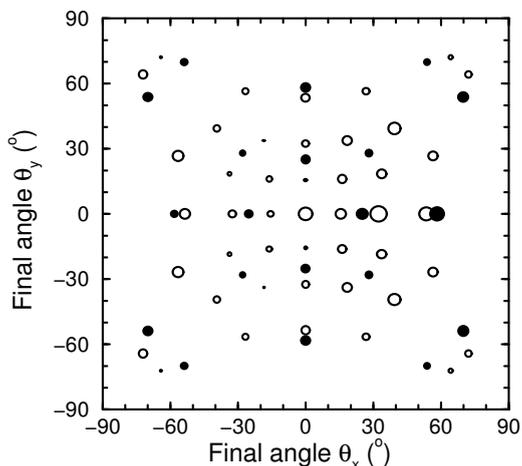


FIG. 2. Angular distribution of the in-plane and out-of-plane of scattering of $\text{H}_2/\text{Pd}(100)$. The initial conditions are the same as in Fig. 1. Open circles correspond to rotationally elastic, filled circles to rotationally inelastic diffraction. The radii of the circles are proportional to the logarithm of the scattering intensity. x denotes the $\langle 0\bar{1}1 \rangle$ direction, y the $\langle 011 \rangle$ direction. The specular peak is the largest open circle.

the experiment the molecular beams are not monoenergetic but have a certain velocity spread. In order to make close contact to experiments we assumed for our results in Figs. 3-5 an initial velocity spread $\Delta v_i/v_i = 0.05$, close to the velocity spread of recent experiments [9].

The theoretical data still exhibit a rather strong oscillatory structure which is a consequence of the quantum nature of hydrogen scattering. We first focus on the specular peak in Fig. 3a). The oscillations at low kinetic energies reflect the opening up of new scattering channels [31]. The first pronounced dip at $E_i = 12$ meV coincides with the opening up of the (11) diffraction peak, the small dip at $E_i = 22$ meV with the opening up of the (20) diffraction channel. The huge dip at approximately 50 meV reflects the threshold for rotationally inelastic scattering. Interestingly, the rotational elastic (10) and (11) diffraction intensities show pronounced maxima at this energy. This indicates a strong coupling between parallel motion and rotational excitation.

Not all peaks in the scattering amplitudes can be unambiguously attributed to the opening up of new scattering channels. Additional structure in the scattering intensities can also be caused by the existence of scattering resonances [19]: molecules can become temporarily trapped into metastable molecular adsorption states at the surface due to the transfer of normal momentum to parallel and angular momentum which resonantly enhances the scattering intensity. Such resonances have been clearly resolved, e.g., in the physisorption of H_2 on $\text{Cu}/(100)$ [32]. However, due to the strong anisotropy

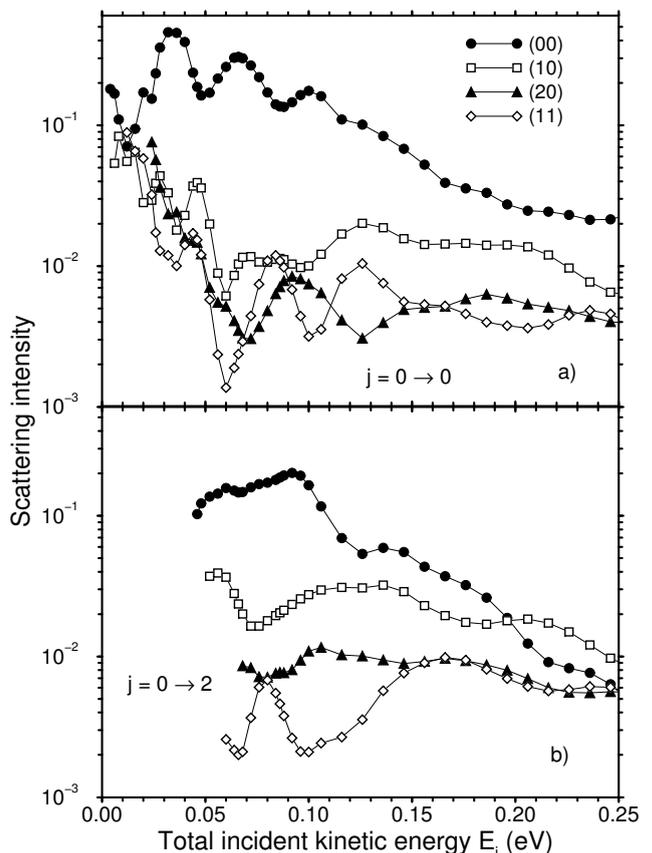


FIG. 3. Scattering intensity versus kinetic energy with an initial velocity spread $\Delta v_i/v_i = 0.05$ for H_2 molecules in the rotational ground state under normal incidence. a) Rotationally elastic $j = 0 \rightarrow 0$ scattering, b) rotationally inelastic $j = 0 \rightarrow 2$ scattering. The intensities are summed over all final azimuthal quantum number m_j .

and corrugation of the $\text{H}_2/\text{Pd}(100)$ PES it is difficult to identify the nature of possible scattering resonances for this system.

Oscillatory structures are known for a long time in He and H_2 scattering [33] and also in LEED [34,35]. For the reactive system $\text{H}_2/\text{Pd}(100)$, however, measuring these oscillations is a very demanding task. They are very sensitive to surface imperfections like adatoms or steps. Due to the high reactivity of this system either an adlayer of hydrogen atoms builds up very rapidly during the experiment or in order to avoid this one has to go to high surface temperatures [36]. Both suppresses the oscillations.

Figure 3b) shows the intensities of rotationally inelastic diffraction peaks. The specular peak is still the largest one, however, some off-specular peaks become larger than the (00) peak at higher energies. This is due to the fact that the rotationally anisotropic component of the potential is more corrugated than the isotropic component [11]. Furthermore it is apparent that the oscillatory structure is somewhat smaller for rotationally inelastic than for rotationally elastic scattering.

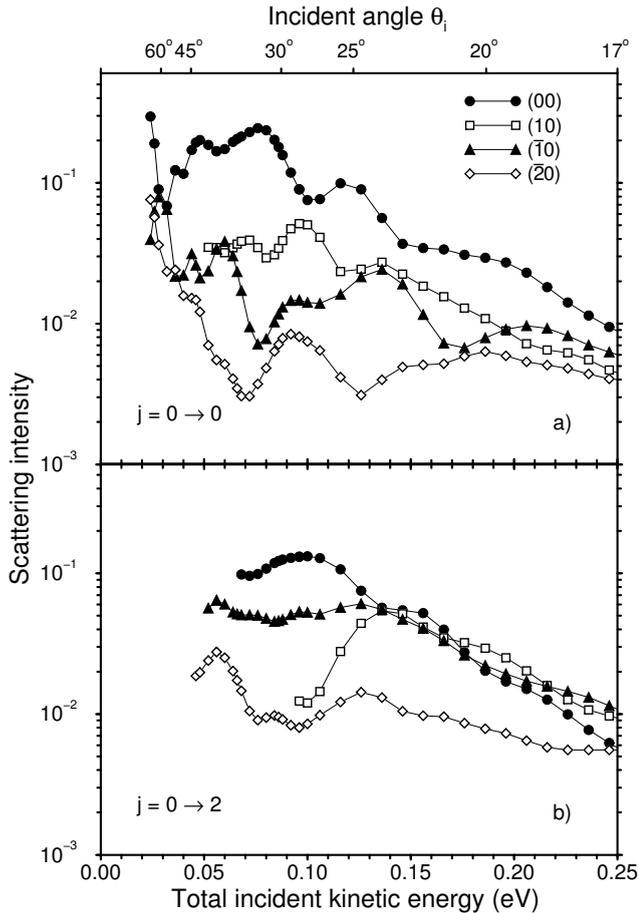


FIG. 4. Scattering intensity versus total kinetic energy with an initial velocity spread $\Delta v_i/v_i = 0.05$ for H_2 molecules in the rotational ground state under off-normal incidence. The incident parallel momentum corresponds to $2\hbar G$ along the $(0\bar{1}1)$ direction with $G = 2\pi/a$. The incident angle is given at the top axis. a) Rotationally elastic $j = 0 \rightarrow 0$ scattering, b) rotationally inelastic $j = 0 \rightarrow 2$ scattering. The intensities are summed over all final azimuthal quantum number m_j .

The results shown in Fig. 4 correspond to a H_2 beam impinging on the Pd(100) surface under off-normal incidence. The initial parallel momentum is $p_{\parallel} = 2\hbar G$ along the $(0\bar{1}1)$ direction. Note that the incident angle decreases with increasing total kinetic energy for constant initial parallel momentum. Only in-plane scattering intensities are plotted. Now the intensities of the off-specular peaks compared to the specular peak are much larger than in the case of normal incidence, which means that the change of parallel momentum in molecule-surface scattering is much more probable for off-normal than for normal incidence. Again a pronounced oscillatory structure for the single diffraction peaks is observed.

One overall trend is evident in Fig. 3 and 4: the scattering intensities of almost all single peaks decrease with increasing kinetic energy as also observed in the experiment

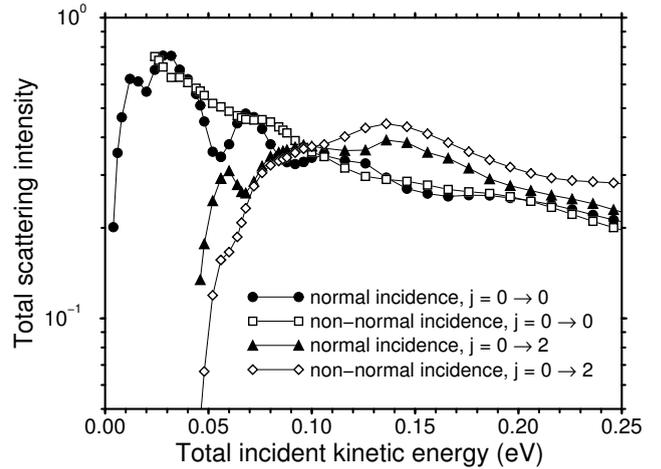


FIG. 5. Total scattering intensity versus total kinetic energy with an initial velocity spread $\Delta v_i/v_i = 0.05$ for rotationally elastic and inelastic scattering at normal incidence and off-normal incidence with initial parallel momentum $p_{\parallel} = 2\hbar G$.

[9], whereby the specular peak decreases more strongly than the off-specular peaks. In ref. [9] the energetic dependence of the scattering intensities is discussed within a Debye-Waller analysis in the impulsive and harmonic approximation [1]; the decrease in the peak height with increasing energy is solely attributed to the interaction with surface phonons. Our analysis, like others before [18–20], shows that there is already a substantial decrease in the intensities for hydrogen scattering at metal surfaces without taking any energy transfer to the phonons into account.

In Fig. 5 we have plotted the total reflection probability for rotationally elastic and rotationally inelastic $j = 0 \rightarrow 2$ scattering, i.e. the sum over all corresponding diffraction peaks. After an initial increase, which corresponds to the decrease of the sticking probability at low energies [21,37], the reflection probabilities generally decrease with increasing energy. For kinetic energies above 0.1 eV the probability of rotationally inelastic $j = 0 \rightarrow 2$ scattering becomes larger than the probability of rotationally elastic scattering. In addition, the rotational excitation is larger for off-normal incidence than for normal incidence. The oscillatory structure of the total scattering intensities is less pronounced (note the different intensity scale) than for the single diffraction peaks, but is still clearly visible, especially the threshold for rotational excitation at normal incidence.

Note that the minimum in the specular peak at $E_i \approx 12$ meV has now turned into a local maximum in the total scattering intensity. This is due to the fact that at this energy not only one scattering channels opens up, but actually four due to symmetry, namely the (10) , $(\bar{1}0)$,

(01) and (0 $\bar{1}$) peaks. The additional scattering intensity in these diffraction peaks over-compensates for the loss of the specular peak in the total scattering intensities.

Although the scattering intensities of the single peak for off-normal incidence also showed a strong oscillatory structure, their sum is rather smooth (see Fig. 5). This can also be understood by symmetry arguments. For an incident angle along the (0 $\bar{1}1$) direction the (10), ($\bar{1}0$), (01) and (0 $\bar{1}$) peaks, e.g., open up at three different energies, for a general incident azimuth even at four different energies. Therefore the effect of the opening up of new scattering channels is significantly reduced for the total scattering intensity compared to normal incidence. As far as quantum oscillations are concerned, it is therefore not reasonable to compare experiments for an angle of incidence of $\theta_i = 15^\circ$ [24] with calculations for normal incidence. Still it should be mentioned that the angles of incidence used in the calculations presented here are larger than $\theta_i = 15^\circ$. However, recent calculations of the sticking probability for $\theta_i = 15^\circ$ that we have performed support our view [29].

In recent four-dimensional dynamical calculations of the dissociative adsorption of the reactive system H₂/W(100) [12], where also the steering mechanism is operative, oscillations in the sticking probability are found, too, but they are much smaller than for H₂/Pd(100). This may be caused by the reduced dimensionality of these calculations. Since only one surface coordinate was considered, the number of degenerate scattering channels opening up is less than in six-dimensional calculations, leading to smaller effects.

In order to observe quantum oscillations we suggest not to determine the whole scattering flux for off-normal incidence as done in ref. [24], but rather monitor the intensity of a single diffraction peak as a function of the kinetic energy. Thus one also avoids to include incoherently scattered molecules due to impurity or multiphonon scattering in the measurements. In our calculations the substrate is held fixed. Substrate motion certainly makes the detection of quantum oscillations more difficult. Since these oscillations have been observed for H₂ scattering at other surfaces [32,33], they should nevertheless also be detectable for H₂/Pd(100) scattering.

The general decrease of the total scattering intensities at higher energies reflects the fact that the sticking probability rises in this energy range so that less molecules are reflected. However, the decrease of the total intensities is much slower than the decrease of the single peaks in Figs. 3 and 4 (note again the different intensity scale). This implies that the decrease in the intensities of the single peaks is partly compensated by the opening up of new scattering channels with increasing kinetic energy. The number of energetically accessible parallel momentum states increases roughly linearly with energy, as does the number of rotational states, so that the number of accessible scatterings states increases quadratically with in-

creasing energy (again neglecting vibrational excitation). Hence the increase of the available phase space for scattering with increasing kinetic energy is responsible for the stronger decrease of the single diffraction peaks compared to the total reflection probability.

IV. CONCLUSIONS

In conclusion, we have performed a six-dimensional quantum dynamical study of the scattering of H₂ from a Pd(100) surface using a potential energy surface (PES) derived from first-principles calculation. The corrugation and anisotropy of the PES lead to strong off-specular and rotationally inelastic diffraction intensities. Strong quantum oscillations in the diffraction intensities as a function of the kinetic energy are obtained. Especially at low kinetic energies they reflect the opening up of new scattering channels with increasing kinetic energy.

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