In-Plane and Out-Plane Diffraction of H\textsubscript{2} from Ru(001)

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**ABSTRACT:** H\textsubscript{2} diffraction from the Ru(001) surface has been measured for incident energies \( E_{\text{i}} = 78–150 \) meV and incidence angles \( \Theta_{\text{i}} = 22.1–64.1^\circ \). In-plane and out-of-plane angular distributions were measured for incidence along [110] and [100] directions. Out-of-plane diffraction channels were found to be predominant for the explored experimental conditions regardless of the incidence direction. An analysis of diffraction intensities reveals that diffraction out of the scattering plane is enhanced for high incidence angles. Diffractive transitions with wavevector change in the surface plane and transversal to the incidence direction \( \Delta K_{\perp} \) were observed to be favored among the out-of-plane diffractive transitions. These features could be reproduced by model calculations of diffraction intensities performed using a three-dimensional soft potential. This suggests that a kinematic effect is responsible for the large out-of-plane intensities observed in experiment, more than any other features of the six-dimensional H\textsubscript{2}-surface interaction potential.

1. INTRODUCTION

The study of the interaction of H\textsubscript{2} with metal surfaces is relevant in many fields of physics and chemistry.\textsuperscript{1–8} Thanks to the lightweight of H\textsubscript{2}, energy transfer processes are easily resolved in the angular distribution of H\textsubscript{2} scattered from a surface. This property has been exploited in a number of discoveries of important fundamental phenomena in molecule-surface scattering. In 1929, experiments on He and H\textsubscript{2} scattering from LiF showed diffraction of the scattered atoms/molecules and, thereby, served to further demonstrate the wave nature of matter.\textsuperscript{9} Early experiments on He and H\textsubcript{2} scattering from LiF also revealed the phenomenon of corrugated mediated selective adsorption (CMSA).\textsuperscript{10} Rotationally inelastic molecule-surface scattering was first observed experimentally in conjunction with diffractive scattering for H\textsubscript{2}–LiF(001)\textsuperscript{11} and HD and H\textsubscript{2}–MgO-(001).\textsuperscript{12} Rotationally mediated selective adsorption (RMSA) was first observed in scattering of HD from Pt(111).\textsuperscript{13}

Diffractive experiments, in which the angular distributions of reflected molecules are analyzed for quantized changes in translational momentum is a fundamental tool in the study of the interaction of atoms and molecules with surfaces.\textsuperscript{14} As it is well-known, helium atom scattering is a common tool to investigate surface properties. In these experiments, the positions of the different diffraction peaks provide detailed information not only on the surface structure but also on the particle–surface interaction. The situation is, in principle, much more complex with a molecule as simple as H\textsubscript{2} because the multidimensional character of the H\textsubscript{2}-surface problem comes into play. Furthermore, even though its stronger interaction with the surface makes diffraction intensities larger than for He, the coupling with the dissociative adsorption channel makes this system an experimental challenge for reactive surfaces, due to the low reflectivities for these systems.

In the last years, a number of studies on H\textsubscript{2} scattering from metal surfaces revealed diffraction patterns in which diffraction out of the scattering plane is much more intense than in-plane diffraction.\textsuperscript{15,16} Furthermore, out-of-plane diffraction was found to be very important, and its importance increases with increasing reactivity. In the case of a nonactivated system like Pd(111), a remarkable feature is the appearance of pronounced out-of-plane diffraction of up to \( 59 \pm 3\% \) of the specular peak intensity, while no diffraction peaks are observed in the scattering plane. For a surface with a low barrier for dissociation like Pt(111), low intensity in-plane peaks were observed, but still the general trend is that out-of-plane diffraction is more important than in-plane diffraction. For H\textsubscript{2} diffraction from the NiAl(110) surface, which has a high barrier for dissociation, the out-of-plane intensity is a few percent of the specular one, indicating a more important role for the out-of-plane diffraction intensity than in the He scattering but lower than for the case of Pt(111) surface.\textsuperscript{17}

These observations are in contrast with reported data for out-of-plane diffraction of helium from close-packed surfaces like...
He−Ni(110)\textsuperscript{18} and He-NiAl(110),\textsuperscript{19} whereby the out-of-plane intensity represents a few percent and a few tenths percent of the specular one, respectively. Surprisingly, diffraction patterns cannot be understood only from differences in surface corrugation along different symmetry directions, since out-of-plane intensities demonstrated to be very large regardless of the crystallographic incidence direction. This effect was explained to be the consequence of a new effect associated with grazing incidence and the periodicity of the potential. This interpretation, based on the periodicity of the potential along the incidence direction, suggests that this effect should also be expected in the scattering of light atoms that approach close enough to the surface.\textsuperscript{15} This model predicted H\textsubscript{2} out-of-plane diffraction to be important for any nonactivated system and for activated ones with barriers for dissociation of the order of the molecular hydrogen incident energies.\textsuperscript{20}

Here, we present new experimental data on diffraction of H\textsubscript{2} from Ru(001). Diffraction intensities were extracted from angular distribution measurements for a variety of incident energies and angles. This dependence will be discussed with special emphasis on the behavior of the out-of-plane diffraction intensities. The final goal is to investigate whether the diffraction pattern of H\textsubscript{2}−Ru(001) is similar to that observed earlier for H\textsubscript{2}−Pd(111)\textsuperscript{15} and H\textsubscript{2}−Pt(111),\textsuperscript{16} in that out-of-plane diffraction dominates over in-plane diffractive scattering. In addition, we will show that this effect can be attributed to a kinematic effect, since it can be reproduced by close-coupling calculations of the diffraction intensities including a three-dimensional interaction potential.

2. EXPERIMENTAL SECTION

A. Experimental Setup. The H\textsubscript{2} diffraction experiments were carried out with the TEAMS (thermal energy atomic and molecular scattering) apparatus located at LASUAM (Laboratorio de Superficies de la Universidad Autónoma de Madrid). A schematic sketch of the TEAMS apparatus is shown in Figure 1. The setup consists of two separate chambers. The source chamber, where the beam is generated, is separated by an ultrahigh vacuum valve from the main chamber in which the sample is prepared and studied. The system is suitable to generate a monochromatic H\textsubscript{2} and He beam by changing the injected gas. The source chamber is three-staged differentially pumped with 4600 L/s liquid nitrogen baffled oil diffusion pumps in each of the first two stages, and a 350 L/s turbomolecular pump in the third stage. The beam is generated by injecting high pressure (P\textsubscript{0} = 20−60 bar) H\textsubscript{2} gas from the nozzle (3) into the first stage through a 10 μm aperture. Diffusion pump ensures background pressure in this stage to remain in the 10^{-3} mbar range for typical operating conditions. The temperature of the gas in the nozzle can be measured and controlled. The nozzle tube is clamped between two cooper blocks that can be cooled down to 100 K with liquid nitrogen. In addition, it can be resistibly heated up to 640 K. Temperature regulation is achieved by a K type thermocouple probe spot-welded to the nozzle and connected to a PID control unit. As a result, the energy for the generated H\textsubscript{2} (He) beam, E\textsubscript{o} can be tuned in the 25−160 (21−134) meV range.

The beam is extracted from the first stage with the skimmer (4). The nozzle-skimmer distance can be adjusted (2) from 5 to 50 mm to optimize the beam intensity. The resulting beam passes through the second stage whose base pressure is in the 10^{-6} mbar range. Collimation of the beam is obtained by a diaphragm whose diameter can be varied with a rotary disk (5) with apertures of different diameters (400−2000 μm). The beam is then mechanically chopped in the third stage (Base pressure 10^{-8} mbar) by a blade rotary moved (6) through a magnetically coupled feedthrough. The chopper disk is circular with 75 mm diameter and four slits 57 mm wide at the disk edge. Beam phase and frequency is registered by means of a LED-photodiode (7) couple. Beam chopping allows phase sensitive detection. The intensity for the beam generated in this way is estimated to be 1 × 10^{14} molecules cm^{-2} s^{-1}, as calculated for an ideal free jet.\textsuperscript{21} The energy spread for the generated beam was estimated to be 7% for E\textsubscript{o} = 78 meV, as judged from the angular spread observed in the H\textsubscript{2} diffraction spectra.

The 18 in. diameter scattering chamber is pumped by a 500 L/s turbomolecular pump reaching a base pressure of typically 5 × 10^{-10} mbar. A liquid nitrogen trap (12) combined with a titanium sublimation pump are used to further decrease background pressure down to the 10^{-11} mbar range. The sample mounted on the sampleholder (9) can be transferred to the main chamber by means of a load-lock system (13). Fast entrance chamber is pumped down by a turbomolecular pump (60 L/s). An ion gun (15), three different dosage valves (11), and a LEED (low energy electron diffraction) system were used to clean and characterize the sample. The manipulator enables sample positioning and orientation with five degrees of freedom. It can be moved in the Z direction by a motor (18) and in the X−Y plane with two micrometric screws (19). Furthermore, the sample can be rotated in the X−Y plane by means of a rotary feedthrough (17), which fixes the angle of incidence Θ_{i} with respect to the surface normal. The azimuthal angle, which determines the incidence direction with respect to the surface lattice vectors, can be varied as well. Two electrical feedthroughs (20,21) are used for sample heating and temperature measurement. The manipulator and, hence the sample holder, can be cooled down by using nitrogen (80 K) or helium (50 K) as cryogenic liquid (22,23). In the present experiments, sample heating was obtained by electronic bombardment and sample temperature,
$\Theta_T$ was monitored with a C type thermocouple spot-welded to the sample.

The H$_2$ angular distributions were recorded with a quadrupole mass spectrometer mounted on a two-axis goniometer. The quadrupole ionization chamber is accessed through a 1.0 mm diameter circular slit located 55 mm away from the sample. The angle subtended by the aperture is, thus, 1.04°. The goniometer can be rotated 200° within the X–Y plane, and 15° out-of-plane. Detector movement is obtained by means of two stepper motors with a minimum step of 0.02° for in-plane and out-of-plane rotation. The quadrupole signal is measured synchronously after filtering with the reference signal from the chopper by means of a lock-in amplifier. Both motors movement and detector signal are fully computer controlled, and angular distributions are usually measured and recorded in this way. Therefore, complete angular distributions could be measured for fixed incident conditions $E_i$ and $\Theta_F$. Furthermore, the incident beam flux is routinely measured and hence absolute detection intensities can be determined. The detection limit of this apparatus is $\sim 3 \times 10^{-3}$ of the incident beam intensity.

**B. Experimental Procedure.** Figure 2 shows the real and reciprocal spaces and their unit cells for the (001) surface of a ruthenium crystal. High symmetry crystallographic directions are shown as well as real and reciprocal unit cell units. Black dashed lines shows in-plane angular distributions. Red, blue, and green dashed lines in (b) indicate the directions corresponding to the out-of-plane diffraction spectra presented in this work.

**Figure 2.** (a) Real and (b) reciprocal spaces for the (001) surface of a ruthenium crystal. High symmetry crystallographic directions are shown as well as real and reciprocal unit cell units. Black dashed lines shows in-plane angular distributions. Red, blue, and green dashed lines in (b) indicate the directions corresponding to the out-of-plane diffraction spectra presented in this work.

Surface temperature was kept to 500 K during diffraction experiments to avoid hydrogen adsorption. Instantaneous coverage on the surface can be estimated assuming that hydrogen desorption for conditions used in the experiments obeys a second order desorption process. The equilibrium coverage is obtained by equaling the desorption rate to the adsorption rate. As stated above, the incident beam flux is of the order of $1 \times 10^{14}$ molecules·cm$^{-2}$·s$^{-1}$. The surface atom density $N_A$ is $2/(\sqrt{3}a_0^2)$ $\sim 1.57 \times 10^{23}$ atoms·cm$^{-2}$, which corresponds to an adsorption rate of 0.13 ML·s$^{-1}$ assuming a sticking coefficient equal to unity. Desorption rate $r_{des}$ assuming that hydrogen desorption is a second order process is given by

$$r_{des} = \frac{\theta^{2}N_A e^{-E_{des}/k_B T_s}}{\nu_{des} N_d}$$  \hspace{1cm} (1)$$

where $\theta$ is the instantaneous coverage on the surface, $k_B$ is the Boltzmann constant, $E_{des}$ is the desorption energy, and $\nu_{des}$ is the pre-exponential factor. From thermal desorption spectroscopy (TDS) experiments, the values for $E_{des}$ and $\nu_{des}$ were found to be 1.3 eV and 3 cm$^3$·s$^{-1}$, respectively.$^{26}$ The instantaneous coverage is obtained by equaling $r_{des}$ to the adsorption rate calculated previously 0.13 ML·s$^{-1}$ in the equation

$$\theta = \left(\frac{r_{des}}{\nu_{des} N_d e^{-E_{des}/k_B T_s}}\right)^{1/2}$$  \hspace{1cm} (2)$$

From the above values, an instantaneous coverage of $2 \times 10^{-2}$ ML is obtained, which can be considered a clean Ru(001) surface for all practical purposes. It should be emphasized that this corresponds to the worst case estimation. The assumption that the sticking coefficient for any coverage is equal to one is clearly an overestimation. The H$_2$ sticking coefficient for zero coverage for this surface has been experimentally determined to be in the range 0.3–0.5 for the beam energies explored in the present experiments.$^{27}$ Therefore, the estimated coverage $\theta = 2 \times 10^{-2}$ ML should be taken as an upper limit.

**3. RESULTS**

In-plane and out-of-plane angular distributions of H$_2$ scattering off Ru(001) were measured systematically for $E_i = 78–150$ meV and $\Theta_F = 22.1–64.1^\circ$. Only elastic diffraction peaks were resolved for the explored experimental conditions. To emphasize the great difference between hydrogen and a noble gas like helium in scattering experiments, we show in Figure 3 measurements of H$_2$ (Figure 3a) and He (Figure 3b) diffraction from Ru(001) for similar experimental conditions. Note that out-of-plane scans for H$_2$ are enlarged $\times 2$ with respect to in-plane angular scans, while
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State of the art in He scattering on Ru(001) for incidence along the [100] direction. In this case, like already observed in H$_2$ scattering experiments on Pt(111) along the [112] direction, the out-of-plane diffraction intensities were much higher than the in-plane ones. Both (10) and (01) diffraction peaks are clearly resolved in the angular distributions and exhibit intensities up to 1 order of magnitude larger than the (1T) and (11) diffraction channels. The out-of-plane diffraction channel (2T) was also clearly resolved for a wide range of experimental conditions. Its intensity is, however, relatively low when compared with the other first order out-of-plane diffraction peaks measured and, thus, it will not be considered in the data analysis of the following section.

For fixed $E_i$, overall diffraction intensities decrease as $\Theta_i$ is increased along both [100] and [110] directions. An explanation from this fact can be given in terms of geometrical corrugation. As the molecule impinges the surface at large $\Theta_i$, the lower parts of the corrugation are not probed. Therefore, the corrugation amplitude seen by the molecule is lower as $\Theta_i$ is increased and, thus, intensities from diffraction peaks other than specular will be lower. The above explanation was found to hold for He scattering on surfaces where experimental diffraction intensities was found to be well reproduced using a Hard-Wall-Corrugation (HCW) model. It is unclear if this can be generally applied for H$_2$ scattering. However, diffraction intensity calculations under the HCW model was found to reproduce quite well the experimental results in some systems. Theory under the HCW approximation

Figure 4. Angular distributions for incidence along [100] direction. Left column plots (a–d) are measurements for $E_i = 113$ meV for several $\Theta_i$ whereas in the right column (e–h) measurements for $E_i = 138$ meV for different $\Theta_i$ are displayed. When resolved, the (21) diffraction peak is labeled. Vertical scale for out-of-plane scans are enlarged ×2.

Figure 5. Angular distributions for incidence along [110] direction. Left column plots (a–d) are measurements for $E_i = 113$ meV for several $\Theta_i$ whereas in the right column (e–h), measurements for $E_i = 150$ meV for different $\Theta_i$ are displayed. Vertical scale for out-of-plane scans is enlarged ×2.

a ×10 enlargement has been used for out-of-plane He angular distributions. Therefore, it can be seen that diffraction intensities for H$_2$ are more than 1 order of magnitude higher than the ones observed for the helium case. This fact is, very likely, a result of the much higher corrugation of the H$_2$–Ru(001) interaction potential compared to the He–Ru(001) system.

Figure 4 shows typical experiments of H$_2$ scattering on Ru(001) for incidence along the [100] direction for different energies and incidence angles. Out-of-plane diffraction peaks demonstrated to be the most intense ones besides the specular peak. In fact, in present experiments, the in-plane diffraction peak (2T) presents very low intensities. All three out-of-plane diffraction peaks (0T), (11), and (01) exhibit intensities higher than in-plane diffraction peaks besides specular. For this incidence direction, the (01) diffraction channel presents the highest intensities for all explored experimental conditions. It is worth noting that the (01) diffraction peak measured along the [100] incidence direction in Ru(001) is geometrically equivalent to the (01) peak observed along the [10T] azimuth on the Pd(111) and Pt(111) surfaces. Previous experimental work demonstrated that the (01) diffractive transition for incidence along [101] direction for these two systems present the highest intensities. In all three cases, this diffractive channel corresponds to momentum transfer in the direction perpendicular to the scattering plane and parallel to the surface plane. In the following section, first order diffraction channels both in and out of the scattering plane were experimentally resolved. In this case, like already observed in H$_2$ scattering experiments on Pt(111) along the [112] direction, the out-of-plane diffraction intensities were much higher than the in-plane ones. Both (10) and (01) diffraction peaks are clearly resolved in the angular distributions and exhibit intensities up to 1 order of magnitude larger than the (1T) and (11) diffraction channels. The out-of-plane diffraction channel (2T) was also clearly resolved for a wide range of experimental conditions. Its intensity is, however, relatively low when compared with the other first order out-of-plane diffraction peaks measured and, thus, it will not be considered in the data analysis of the following section.

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for the elastic diffraction and RID intensities for H₂ was developed by Garibaldi et al. Calculations within the HCW model for the case of molecular scattering show that both elastic and inelastic diffraction probabilities can be roughly accounted for by a hard-wall scattering mechanism. Although, obviously the problem cannot be properly described by the HCW approximation, some diffraction intensity features observed in present experiments can be predicted already within such a simple picture.

4. DISCUSSION

A. Intensity Analysis. Large out-of-plane diffraction intensities demonstrated to be a ubiquitous trend observed in present experiments. An analysis of the diffraction intensities obtained for H₂ scattering experiments on Ru(001) will be carried out in the following. Present experiments were performed with constant temperature Tₛ = 500 K. Therefore, diffraction intensity losses due to atomic thermal vibrations should be considered.

Thermal attenuation is quantitatively different for different experimental conditions (Eᵢ, Θᵢ) and for each diffraction channel. The Debye—Waller model was found to be obeyed by H₂—Ru(001) in present experiments. Therefore, one possible procedure to subtract thermal diffraction intensity losses would be to obtain the Debye—Waller factor from diffraction intensity versus Tₛ measurements and extrapolate the experimental intensities to 0 K. This method has been used to make a theory-experiment comparison and will be published elsewhere. A different way to filter out thermal contribution is to normalize experimental intensities to one diffraction peak. As zero and first order diffraction peaks should present to a good approximation about the same Debye—Waller factor, thermal attenuations are approximately canceled by normalizing diffraction intensities.

Figure 6 shows intensities for first order diffraction peaks versus Θᵢ for both directions and Eᵢ = 78, 113, and 150 meV. Intensities for out-of-plane diffraction peaks have been doubled since equally intense diffractive transitions are expected due to surface symmetry, for example, for incidence along [100] direction, (T0) and (TT) Bragg peaks present the same intensity. The first general trend observed for both directions and all explored energies is the overall decreasing of the diffraction intensities for all first order diffraction intensities, as was already put into manifest by the angular distributions (Figures 4 and 5) shown in the preceding section. It was also evident from the angular distributions that measured out-of-plane diffraction intensities are much higher than in-plane intensities. For the [110] direction and near normal incidence angle, the (11) and (TT) diffraction peaks (in-plane forward and backscattering, respectively) present about the same intensity than (T0) and (01). For experiments with higher Θᵢ the out-of-plane intensity is nearly 1 order of magnitude higher than the (TT) Bragg peak.

For measurements along [100] direction, intensities for (01), (T0) and (11) whose final angles are out of the scattering plane, are plotted. Intensities for the in-plane diffraction peak closest to specular, (T1) were found to be very low. This diffraction channel was resolved experimentally only for a few experimental conditions. In addition, Debye—Waller factor for this diffraction peak cannot be considered the same than for first order and specular diffraction peaks. For all these reasons (T1) was not taken into account in the discussion. Although no extensive information about in-plane intensities is available from the experiments, the relative intensities for all three (01), (T0), and (11) diffraction channels will be discussed in the following. For the Eᵢ and Θᵢ range explored in the experiments, the (01) diffractive transition was found to exhibit the largest intensity. As the incident angle is increased, all diffraction intensities decrease as was already discussed for the [110] direction. However, the (T0) Bragg peak normalized intensity decreases at a higher rate than the normalized intensity for (01) diffraction peak. The difference is small for incident energy of 78 meV, but it is quite large for the measurements done at 113 and 150 meV.

Another interesting feature is observed for the (11) diffraction peak for the [100] direction. For Eᵢ = 78 meV it presents the lowest intensity of the three diffraction peaks under consideration, while for Eᵢ = 113 meV, its intensity is larger than the backward (T0) diffraction peak. Finally, for an incident energy of 150 meV, it exhibits larger intensity than the (T0) peak for all explored Θᵢ. In other words, as Eᵢ is increased, the out-of-plane forward scattering is enhanced.

The importance of the out-of-plane with respect to in-plane diffraction intensities can be presented in a straightforward way for the [110] direction by defining the ratio Iᵢ¹¹ as the sum of all the out-of-plane first order diffraction intensities divided by the in-plane first order diffraction intensities, namely

\[ I_{ik}^{11} = \frac{2 \cdot I_{01} + 2 \cdot I_{T0}}{I_{T1} + I_{TT}} \] (3)

Values for Iᵢ¹¹ versus Θᵢ are given in Figure 7 for three different energies. In the first place, it can be seen that except for near normal incidence, Iᵢ¹¹ values are in the 5—20 range, which means that out-of-plane intensity is around 1 order of magnitude larger than the in-
such as (11) and (01) transitions that imply a momentum transition in the scattering plane. In contrast it is not zero in the transversal direction. Involving a momentum transfer in the perpendicular direction, that in the surface plane, the momentum of the particle is assumed to be large compared with momentum change due to the interaction with the surface. It can be demonstrated that the momentum change in the direction of the particles’ velocity is zero due to the periodicity of the potential. In contrast it is not zero in the transversal direction. Therefore, for incidence along [110], those diffraction channels involving a momentum transfer in the perpendicular direction, that is, (T0 and (01), are favored with respect to those diffraction transitions that imply a momentum transition in the scattering plane such as (11) and (TT).

In Figure 7 it should be kept in mind that the closing up of diffraction channels occurs as we go to grazing incidence. This is, very likely, the reason for the fall off at the highest \( \Theta_i \) and \( E_i = 150 \) meV, which is a consequence of the closing up of the (01) diffraction channel, as can be seen in Figures 6 and 5g.h. However, it cannot be argued that the increasing of \( \Delta R_{10}^{10} \) can be explained from this fact alone. As shown in Figure 6, (TT) and (T0) are open diffraction channels for the \( \Theta_i \) range of the experiments and it can be seen that the (TT) diffraction intensity decreases at a faster rate than the (T0) intensity.

The in-plane diffraction for the [100] incidence direction cannot be used to define an out-of-plane to in-plane ratio like was done for the [110], because in-plane diffraction intensities were found to be very low. However, important information can still be extracted from the three out-of-plane peaks measured for this incidence direction. The (01) diffraction channel, unlike the other two, involves only a wavevector change in the surface plane and transversal to the incidence direction \( \Delta K_i \). For the other two diffraction transitions under consideration (T0 and 01) a not null wavevector change along the incidence direction \( \Delta K_i \) is produced as well. For this reason, a ratio \( R_{10}^{100} \) is defined as

\[
R_{10}^{100} = \frac{I_{01}}{I_{00} + I_{11}}
\]  

The ratio defined in eq 4 has been plotted in Figure 8 versus incidence angle for different \( E_i \). It can be seen that \( R_{10}^{100} \) increases monotonically with \( \Theta_i \). This is an indication of the preferential direction for wavevector change among the out-of-plane diffraction peaks. The experimental results show that \( \Delta K_i \) is enhanced with respect to \( \Delta K_i \) as the incidence angle is increased. When increasing \( \Theta_i \) to grazing incidence, diffractive transitions involving only \( \Delta K_i \) are favored with respect to other transitions for which a wavevector change \( \Delta K_i \) is needed. It is also remarkable that, as energy is increased, this effect is more important.

B. Model Calculations. Calculations of diffraction intensities with a model potential were carried out to get some insight on the experimental observations. The main aim of such calculations was to see whether the trends observed for out-of-plane diffraction intensities at different incident energies and angles can be reproduced by three-dimensional calculations, that is, to see whether this behavior can be traced back to a pure kinematic effect. However, it should be stressed that no fit to experimental intensities is intended.

A Fourier expansion was used for 6-fold symmetry model potential

\[
V(x, y, z) = V_{00}(z) + A_{10}e^{-\alpha_{10}^2}(F_{10} + F_{01} + F_{11} + F_{0-1} + F_{-10} + F_{-1-1})
\]

where

\[
F_{ij} = \cos \left[ \frac{2\pi}{\bar{a}} \left( ix + y \left( \sqrt{3} \left( \frac{j}{2} \frac{i}{3} \right) \right) \right) \right]
\]

and a Morse-type potential was used for \( V_{00} \)

\[
V_{00} = D(e^{-2\alpha_0(z-z_0)} + 2e^{-\alpha_0(z-z_0)})
\]

the following values where used for the different constants for the calculations shown here

\[
A_{10} = 100 \text{ meV}; \quad \alpha_{10} = 1.8 \text{ Å}^{-1}; \quad D = 8 \text{ meV}; \quad \alpha_{00} = 1.0 \text{ Å}^{-1}; \quad z_0 = 3.5 \text{ Å}; \quad |\bar{a}| = 2.71 \text{ Å}
\]

Diffraction intensities were calculated by means of the Close-Coupling method. The coupled equations were solved using the MOLSCAT33 code with the algorithm developed by Manolopoulos and Wyatt.34 Figure 9 shows the normalized diffraction probabilities as a function of incidence angle \( \Theta_i \) obtained for incidence along both high symmetry directions, and for \( E_i = 50, 90, \) and 130 meV.

An overall decreasing of diffraction probabilities with increasing angle is observed for all channels as observed experimentally.
Interestingly, the out-of-plane diffractive channels present the highest intensities. For incidence along the [110] direction, out-of-plane diffraction probabilities ((100) and (01) channels) were found to be higher than in-plane diffraction probabilities for all explored incidence conditions. Furthermore, the in-plane diffraction probabilities were observed to decrease faster than out-of-plane diffraction probabilities. The same trend was found for calculations with incidence along [100]. Out-of-plane diffraction probabilities were found to be higher than in-plane diffraction probabilities for incidence along this direction (not shown).

### Figure 9.
Normalized diffraction intensities from model calculations vs angle for $E_i = 50, 90,$ and $130$ meV along [110] (left panel) and [100] (right panel) incidence directions.

### Figure 10.
Ratio $I_{110}^{100}$, as defined in eq 3, from model calculations against incidence angle $\Theta_i$ for different energies.

### Figure 11.
Ratio $I_{110}^{100}$, as defined in eq 4, from model calculations against incidence angle $\Theta_i$ for different energies.

Interestingly, the (01) diffraction probability was observed to decrease at a slower rate than for other first order out-of-plane diffractive transitions, as observed experimentally. The $I_{110}^{110}$ and $I_{100}^{100}$ ratios, as defined in eqs 3 and 4, obtained using the intensities from the model calculations are presented in Figures 10 and 11. As observed experimentally, both ratios increase with increasing angle. Furthermore, the effect is more pronounced for higher energies, as observed in the H$_2$/Ru(001) experiments.

The above trends were observed to hold for calculations using a variety of 6-fold model potentials ($A_{10} =$ 100–800 meV; $|a| = 2.71–2.77$ Å) as well as for model potentials with 4-fold symmetry. Although the diffraction intensities of the different diffraction channels were observed to depend on the details of the potential employed, pronounced out-of-plane diffraction intensities for high incidence angles were obtained in all cases. In particular, those diffractive transitions that involve a $\Delta k$ wavevector change were found to be favored with respect to those in which a $\Delta k$ wavevector change is needed, as observed experimentally for H$_2$–Ru(001). These results indicate that the dominant features observed in experiment are mainly due to the kinematics of the three-dimensional scattering process and not to the details of the potential.

H$_2$ diffraction experiments on Pd(111)15 and Pt(111)16 were reported previously, finding high diffraction intensities out of the scattering plane. Furthermore, the diffraction intensities were reproduced with ab initio calculations. For the case of the H$_2$–Pd(111) system the results were explained considering the grazing incidence model. The present experiments are compatible with this interpretation. Furthermore, the model calculations presented here reproduce the main trends found in H$_2$ diffraction experiments independently of the used potential, indicating that prominent out-of-plane diffraction intensities for high incident angles is a general phenomenon for H$_2$ diffraction from clean metal surfaces with no or low barrier for dissociation.20

### 5. CONCLUSIONS

We have performed H$_2$ diffraction experiments from the Ru(001) surface for incident energies $E_i =$ 78–150 meV and angles of incidence $\Theta_i = 22.1–64.1^\circ$, for incidence along [110] and [100]. Elastic diffraction channels both in and out of the scattering plane were resolved while no inelastic diffraction transitions were obtained. As in the case of H$_2$ diffraction experiments from Pd(111) and Pt(111) surfaces, predominant out-of-plane diffraction was found regardless of the incidence
direction. An analysis of the diffraction intensities shows that this effect is more pronounced for high incidence angles. Specifically, diffractive transitions with wavevector change in the surface plane and transversal to the incidence direction ΔK∥ were observed to be favored among the out-of-plane diffractive transitions. Model calculations with a variety of three-dimensional potentials were found to reproduce the above observations, suggesting that this is very likely related to a pure kinematic effect, more than to other features of the six-dimensional PES. Indeed it is remarkable that even if the H₂ diffraction from nonactivated surfaces is a multidimensional problem, the experimental observation can be explained qualitatively with a three-dimensional model.

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■ REFERENCES