High-resolution elastic and rotationally inelastic diffraction of D$_2$ from NiAl(110)

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High-resolution angular distributions of D$_2$ scattered from NiAl(110) have been measured at incident energies between 20 and 150 meV. The measurements were performed along the [110] azimuth using a high sensitivity time-of-flight apparatus, which allows the recording of diffraction channels not previously studied, including out-of-plane rotationally inelastic diffraction peaks. The attenuation of both elastic and rotationally inelastic diffraction intensities with surface temperature was found to follow a Debye–Waller model. The time-of-flight data analysis allowed us to assign unequivocally the different transition probabilities to each final state. In this way, 0→2, 2→0, and 1→3 transition probabilities were observed, covering relative intensities over two orders of magnitude. In the energy range investigated, the 0→2 transition was found to be a factor of 2–3 larger than the 2→0 one, which lies a factor of 10 above the 1→3 transition probability.

I. INTRODUCTION

The internal molecular degrees of freedom play a decisive role in the interaction dynamics of molecules with solid surfaces. For the case of H$_2$, it has been shown that vibrational energy reduces the effective translational energy threshold for dissociative adsorption, favoring dissociation both in activated systems and in reactive surfaces. The rotational state of the molecules also affect the dissociation probability, as it has been shown for the H$_2$/Pd(111), H$_2$/Pd(100), H$_2$/Pt(110), and H$_2$/Rh(111) systems, where the dissociation probability decreases when the quantum rotational number $j$ is increased.

Rotational effects in dissociation dynamics were first observed in recombinative desorption experiments of H$_2$ and D$_2$ from Cu(110) and Cu(111) and extensively investigated for Cu(111). In this system, the dissociation probability of the H$_2$ molecule shows a strong dependence on the orientation of the molecular axis ($m_j$). The dissociation probability is higher for molecules colliding with its axis parallel to the surface ($|m_j| = j, \text{helicopter}$) than for molecules impinging with its axis perpendicular to the surface ($|m_j| = 0, \text{cartwheel}$). This feature suggests the possibility of controlling the reaction rate of some important reactions in heterogeneous catalysis through optimal geometry and initial (vibrational and rotational) conditions. Unfortunately, despite the practical importance of this effects, the fundamental knowledge of the process that ultimately determines the result of the interaction continues to be limited.

Molecular beam-surface scattering experiments offer an excellent opportunity to study the influence of molecular internal degrees of freedom in the interaction, and can also be used as a precise test for theoretical models. With this type of experiments, the coupling between the internal molecular degrees of freedom (especially HD) and the interaction potential, surface phonons, and temperature has been studied. For the scattering of H$_2$ and D$_2$ from metallic surfaces, however, fewer experiments have been performed. Previous studies include Ni(110) and Cu(100), which can be considered as representative examples of systems with a low and a high barrier, respectively, to dissociative chemisorption. Quantum calculations based in density functional theory (DFT) determined potentials are still far from agreement with experiment as long as rotationally inelastic diffraction (RID) is concerned. In the case of D$_2$/NiAl(110), a preliminary comparison of some experimental results (obtained using a setup which allows measuring absolute diffraction intensities for a given incidence angle) with quantum calculations seems to agree to a great extent for elastic diffraction, but calculations fail to predict RID probabilities. In the cited work, the main difficulty in the analysis of the intensities came from the fact that for some energy regions, RIDs could not be properly resolved due to the overlap of the final scattering angles. Since it has been argued that this limitation could be the origin of the discrepancy between theory and experiment, there is a need for high-resolution data on this system.

An additional goal of performing studies like the current one is also to see whether a general trend can be found in the behavior of RID peak intensities on different model surfaces.
similar to the main trends already observed for elastic diffraction intensities (where, for instance, out-of-plane diffraction has been found to increase with increasing reactivity\textsuperscript{33}). This kind of conclusions is essential to provide a more general, qualitative picture of the interaction of H\textsubscript{2}/D\textsubscript{2} with metal surfaces.

In our current work, we present diffraction experiments performed with a high-resolution, time-of-flight apparatus which has been recently transferred from the group of Toennies in Göttingen to the Surface Science Laboratory at the Universidad Autónoma de Madrid. We show that the high angular resolution of the employed apparatus, combined with the possibility of carrying out time-of-flight (TOF) measurements, allows the study of rotational transitions not previously observed in D\textsubscript{2}/NiAl\textsubscript{110\textsuperscript{2}}\textsuperscript{11} over a wide range of incident energies.

II. THE D\textsubscript{2}/NiAl\textsubscript{110\textsuperscript{2}} SYSTEM

NiAl crystallizes in a CsCl structure with a lattice constant of $a=2.89\ \text{Å}$.\textsuperscript{34} The (110) surface termination has an equal number of Ni and Al atoms in the unit cell (Fig. 1) and exhibits a rippled relaxation in which the rows of Ni atoms are contracted toward the bulk by roughly 6% of the bulk layer spacing (~2 Å), while the rows of Al atoms are expanded into the vacuum by 5%.\textsuperscript{35,36} Molecular hydrogen adsorbs and dissociates on clean NiAl(110) through an activated process with a minimum energy barrier lower than for H\textsubscript{2}/Cu, which is usually taken as a model system for activated adsorption. The activation barrier for dissociation strongly depends on the coordinates over the unit cell (~0.3 eV over the Ni atoms and ~1 eV over the Al atoms).\textsuperscript{37} This different local reactivity has been theoretically to strongly affect the interaction dynamics of H\textsubscript{2} with the surface.\textsuperscript{38} The sticking curve has a typical S-like shape, and no significant differences between H\textsubscript{2} and D\textsubscript{2} beams were observed at the same nozzle temperature.\textsuperscript{39} Therefore, in the energy range covered by our experiment, the H\textsubscript{2} and D\textsubscript{2} dissociation probabilities can be considered negligible.

III. EXPERIMENTAL DETAILS

The experiments have been performed using a high-resolution He atom time-of-flight spectrometer initially developed for measuring surface phonon dispersion curves.\textsuperscript{40} It has been transferred a few years ago from Toennies’ group in Göttingen to our laboratory in Madrid. A schematic of the apparatus used in the experiment is depicted in Fig. 2.

Basically, it consists of three main units: the source chamber, the scattering chamber, and the TOF detector chamber. For beam generation, ultrahigh purity gases at high pressure (typically between 30 and 130 bars) are expanded into vacuum through a 10 \textmu m diameter Pt nozzle. In order to avoid nozzle clogging, the gas passes through a liquid nitrogen cooled filter. The He beam energy can be continu-
For the case of D$_2$, we estimate D$_2$ scattering from NiAl from a stagnation pressure of 55 bars. These investigations demonstrated directly that the rotational populations of highly expanded molecules follow nearly a Boltzmann distribution which can be characterized by an effective rotational temperature $T_R$, which depends on the source temperature $T_0$. The relation between $T_R$ and $T_0$ involves the parameter $P_0d$, where $d$ is the nozzle orifice diameter and $P_0$ is the stagnation pressure. The values used in the present work are listed in Table I.

Concerning vibrations, due to the large spacing between the vibrational levels of the D$_2$ molecule, it can be safely stated that more than 99% of the molecules are in the $v=0$ state for incidence energies $E_i < 200$ meV.

The NiAl(110) surface was prepared in UHV by repeated cycles of 1 keV Ar$^+$ sputtering at a surface temperature of $T_S=450$ K followed by annealing at $T_S=1150$ K. The cleanliness of the sample was tested by the Auger spectroscopy. This procedure led to excellent He diffraction patterns (Fig. 3), which are representative of a clean and well ordered surface.

IV. RESULTS
A. In-plane diffraction

Figure 4 shows an in-plane angular distribution of D$_2$ molecules scattered from the NiAl(110) surface along the [110] azimuth at a surface temperature of $T_S=100$ K, to reduce the multiphonon background in the scattering experiments. The beam energy was $E_i=86$ meV. The spectrum shows a variety of RID peaks, whose nature was identified

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TABLE I. Fractional populations (in percent) of the rotational levels $j_i$ for n-D$_2$ beams for stagnation condition $P_0d$=41.25 Torr cm and source temperature $T_0$, estimated from effective beam rotational temperatures $T_R$ as reported in Ref. 41.

<table>
<thead>
<tr>
<th>$E_i$ (meV)</th>
<th>$T_0$ (K)</th>
<th>$T_R$ (K)</th>
<th>$j_i=0$</th>
<th>$j_i=1$</th>
<th>$j_i=2$</th>
<th>$j_i=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>300</td>
<td>99</td>
<td>48.7</td>
<td>32.3</td>
<td>18.0</td>
<td>1.0</td>
</tr>
<tr>
<td>95</td>
<td>334</td>
<td>115</td>
<td>43.5</td>
<td>31.6</td>
<td>23.1</td>
<td>1.8</td>
</tr>
<tr>
<td>108</td>
<td>380</td>
<td>138</td>
<td>37.7</td>
<td>30.2</td>
<td>29.0</td>
<td>3.1</td>
</tr>
<tr>
<td>120</td>
<td>422</td>
<td>159</td>
<td>33.4</td>
<td>28.8</td>
<td>33.2</td>
<td>4.6</td>
</tr>
<tr>
<td>133</td>
<td>468</td>
<td>184</td>
<td>29.8</td>
<td>27.1</td>
<td>36.8</td>
<td>6.2</td>
</tr>
<tr>
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<td>492</td>
<td>198</td>
<td>28.3</td>
<td>26.3</td>
<td>38.4</td>
<td>7.0</td>
</tr>
<tr>
<td>149</td>
<td>525</td>
<td>216</td>
<td>26.5</td>
<td>25.2</td>
<td>40.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>

FIG. 3. Angular distribution of He scattered from the NiAl(110) surface along the [110] azimuth at a surface temperature $T_S=200$ K. The incidence beam energy was $E_i=69$ meV.
by TOF measurements. The position of these peaks can be obtained from the equations of conservation of parallel momentum and energy,

$$K_f - K_i = G,$$

$$E_f - E_i = \Delta E_{\text{rot}},$$

where $K_f$ and $K_i$ are the parallel components of the outgoing and incident wavevectors, respectively, $G$ is a surface reciprocal lattice vector, $E_f$ and $E_i$ are the final and incident beam energies, and $\Delta E_{\text{rot}}$ is the rotational transition energy ($E_{ji} - E_{jf}$). As a result of nuclear spin statistics,\(^4^3\) the even and odd $j$ states are not coupled and transitions between the even and odd rotational levels are strongly forbidden ($\Delta j = 0, \pm 2$). For D$_2$, the rotational energies are $\Delta E_{\text{rot}} = -22.2$ meV for a $j_i = 0 \rightarrow j_f = 2$ rotational transition and $-36.9$ meV for the $j_i = 1 \rightarrow j_f = 3$ transition.\(^4^4\)

Apart from elastic processes, including first and second order diffractions, several RID peaks are present. In particular, the ($j_i = 0 \rightarrow j_f = 2$) rotational transition coupled to the (30), (20), (10), (00), and (10) channels can be observed. Inelastic peaks for excitation to higher rotational levels lie at higher final scattering angles $\Delta \Theta_f$ with respect to their associated elastic peaks and at lower angles for de-excitation. A preliminary inspection of the spectrum of Fig. 4 shows that the intensities of these channels do not seem to be connected with the intensity of its parent elastic peak, but with its angular position. Thus, for example, the intensity of the (10):02 peak is higher than the intensity of the (00):02 channel, in spite of the large specular reflectivity. This trend has also been observed in the scattering of D$_2$ from Ni(110).\(^2^5\)

The intensity of the (20):13 and (10):13 channels is relatively high, although the energy transfer involved is high ($|\Delta E_{\text{rot}}| = 36.9$ meV). Finally, rotational de-excitation are also possible and the (10):20, (00):13, (10):20, and (20):20 channels can be observed.

The large differences observed in the width of the peaks shown in Fig. 4 can be explained by the energy dependence of the final scattering angle of the different RID peaks. For instance, it can be seen that the width of the (10):20 and (20):02 RID peaks is smaller than the width of the corresponding elastic (10) and (20) peaks.

Figure 5 shows the final scattering angle for elastic and rotationally inelastic channels along the [110] azimuth as function of the incidence energy. Here we can see that the angular position for the (20):02 channel, for instance, is nearly independent of energy for $E_i > 60$ meV. This effect, usually called kinematic rotational focusing,\(^4^5\) cancels the energy contribution to the broadening of the peak and, as a consequence, the width of the peak is similar to the specular one.

Figure 6 shows a series of angular distributions of D$_2$ scattered from NiAl(110) at incidence energies between 24 and 146 meV. For energies below 24 meV only elastic diffraction can be seen. These spectra show a dominant specular peak, as expected for low corrugated surfaces.\(^4^6\) At $E_i = 24$ meV the (10):02 peaks are kinematically allowed and can be observed around $\Delta \Theta_f = 18^\circ$.

The peaks (20):02, (10):02, and (00):02, involving ($j_i = 0 \rightarrow j_f = 2$) rotational transitions can be observed for $E_i > 85$ meV. In this energy range, rotational transitions ($j_i = 1 \rightarrow j_f = 3$) are also possible and, in particular, the (20):13 channel is visible over the whole energy range. In the $E_i = 86$ meV angular distribution, the (10) and (00):02 peaks overlap in the same scattering angle, as it can be checked in Fig. 5. This also occurs for the (20):13, whose final scattering angle is the same (within experimental resolution) that the (00):20 peak in the range of 100–115 meV. In that cases, TOF measurements allow us to separate the contribution of each channel to the total intensity gathered at that final angle.

One of these measurements is shown in Fig. 7. The central peak (DE) is the so-called diffuse elastic peak, which results from the scattering of molecules from defects and it is usually employed to set the zero in the energy transfer scale. The left hand side peak is due to molecules that have gained the translational energy corresponding to a ($j_i = 2 \rightarrow j_f = 0$) rotational de-excitation. Finally, the peak on the right corre-
sponds to molecules undergoing a \((j_i = 1 \rightarrow j_f = 3)\) rotational transition. The fitting of the spectrum provides the contribution of each channel to the total intensity measured at \(\Delta \Theta_f = -3.5^\circ\).

### B. Out-of-plane diffraction

Recent experimental studies, supported by classical dynamics calculations, have demonstrated that out-of-plane diffraction is important for \(\text{H}_2\) and \(\text{D}_2\) molecules.\(^{33,47,48}\) For this reason, in this energy range, out-of-plane diffraction has been also measured.

Figure 8 shows a series of out-of-plane angular distributions measured at \(T_S = 100\) K. The incidence energy varies from \(E_i = 87\) to \(E_i = 141\) meV. Each spectrum has been measured for a fixed out-of-plane angle \(\Phi\) (tilt), rotating the sample by an angle \(\Delta \Theta_f = \Theta_f - \Theta_{SD}/2\) away from the specular. For elastic scattering, the parallel wave vector transfer to the surface in this setup can be written as\(^{49}\)

\[
\Delta K_x = 2k_i \sin(\Delta \Theta_f) \cos\left(\frac{\Theta_{SD}}{2}\right),
\]

\[
\Delta K_y = k_i \sin(\Phi) \left[ \cos\left(\frac{\Theta_{SD}}{2} + \Delta \Theta_f\right) + \cos\left(\frac{\Theta_{SD}}{2} - \Delta \Theta_f\right) \right],
\]

where \(k_i\) is the incident wave vector. Since \(\Delta K_y\) depends on both \(\Phi\) and \(\Theta_f\) angles, out-of-plane peaks cannot be gathered in the same angular distribution for a fixed tilt angle. This fact is illustrated on the top of Fig. 8, which shows, for instance, that first order out-of-plane diffraction peaks appear slightly further apart in tilt angle for larger values of \(\Delta \Theta_f\).

The left column of Fig. 8 shows a series of angular distributions for different incidence energies, where the \(\Phi\) angle has been chosen to maximize the (01) peak. In the right column, the tilt angle was fixed to maximize the \((\overline{1}1)\) peak. For each energy, an in-plane angular distribution was also measured, which allows for direct comparison of in-plane and out-of-plane intensities. For lower incident energies it was not possible to measure out-of-plane peaks. Below \(E_i < 87\) meV, first order out-of-plane diffraction requires larger tilt angles which cannot be achieved with our current setup. Rotational transitions \((j_i = 2 \rightarrow j_f = 0)\) could not be resolved in the complete energy range.
V. DIFFRACTION PROBABILITIES

The diffraction peak intensities were determined by fitting Gaussian profiles to the peaks of angular distributions measured for a given energy, $E_i$, and by averaging their integrated intensity over several measurements. The absolute transition probability from an initial state $j_i$ to a final rotational state $j_f$ coupled to the reciprocal lattice vector $G_{mn}$ can be calculated from the expression:

$$
\Phi \Rightarrow (01) \\
\Phi \Rightarrow (11:02)
$$

FIG. 8. Out-of-plane angular distributions for D$_2$/NiAl(110) along the [110] azimuth measured at different incidence energies $E_i$. The surface temperature was $T_S = 100$ K.
The exponential factor accounts for the thermal attenuation of intensities expected from the Debye–Waller model.51–53

Expression (3) gives the experimental probability averaged over the magnetic quantum number \( m_j \), which cannot be measured in the experiment. Since the present experimental setup does not allow measuring the incident beam intensity, in our analysis, the probabilities are always expressed as a probability ratio, relative to peaks appearing in the same angular distribution. RID channels are normalized with respect to the elastic channel (10),

\[
P(00) = \frac{I(00)}{I_{\text{elastic}}},
\]

with \( P(10) \) defined as

\[
P(00) = \frac{I(00)}{I_{\text{elastic}}}.\]

This approach significantly suppresses the error in the extrapolation of probabilities to 0 K. Although correction for different incident angles should still be made for each peak, the maximum error estimated from the Debye–Waller contribution for peaks in the \([-15^\circ–15^\circ]\) range is lower than 20%.

To further support this statement, in Fig. 9 the surface temperature dependence of RID intensities is shown for a fixed beam energy \( E_i = 86 \text{ meV} \). The effect of the crystal temperature is to increase the multiphonon background, while diffraction intensities for different elastic and RID channels are equally attenuated. This behavior also extends for the whole energy range explored, where no significant broadening or shifting of the peaks was measured. This observation indicates, in accordance with previous work,55 that phonons can be neglected in theoretical models of diffraction from metal surfaces.

**VI. DISCUSSION**

Figure 10 shows the normalized scattering probabilities to each final state \((mn;ij)\) in logarithmic scale for both in-plane and out-of-plane channels. Only channels which appreciable intensities in the complete energy range are shown. In the in-plane data, we see that the \((10):02\) is the predominant RID channel and it is nearly independent of the incidence energy. In contrast, the \((00):02\) scattering probability increases from 0.3 to 4.5 in this energy range. We see that high rotational transition probabilities are observed in the energy range studied (i.e., at incident energies well below the dissociative chemisorption barrier), as also reported for \(D_2/Cu(100)\).25

Previous theoretical and experimental studies showed that in \(D_2/NiAl(110)\) elastic and rotationally inelastic diffraction are nearly independent of incident angle. This means that the ratio between RID intensities should remain constant for different incident angles. However, the behavior of the \((00):02\) channel with energy might be related with kinematical conditions. As it is evident from Fig. 5, the final angular position \(\Delta \Theta_f\) of this channel decreases faster (it gets closer to the specular peak) with increasing energy than oth-
ers do. Attempts to fit the normalized intensities with the eikonal approach failed, in accordance with previous work. Nonetheless, it was always possible to choose a range of surface corrugations between 0.18 and 0.27 Å so that relative intensities of RID peaks qualitatively resemble the experimental data.

The out-of-plane elastic diffraction and RID probabilities are plotted in Fig. 10(b). The final probabilities have been normalized to the in-plane (10) channel probability $R(10)$. It can be seen that out-of-plane RID probabilities $R(11:02)$ and $R(01:02)$ monotonically increase with energy, while the elastic $R(01)$ probability remains nearly constant in this energy range.

Classical calculations performed using DFT-based potential energy surfaces (PESs) showed that the closest approach distance of $H_2$ molecules to the NiAl(110) surface lies between $Z=2.5$ and 2.8 Å. The corresponding PES presents a repulsive behavior in the entrance channel, and as a consequence, molecules impinging on the surface with a perpendicular energy of $\sim 100$ meV find a slightly corrugated hard-wall-like potential in that region. A similar behavior is expected for Cu(001), a surface which also presents a large barrier toward dissociation of $H_2$. Therefore, the scattering of $H_2$ from these surfaces resembles very much the scattering process of He atoms from metal surfaces, whereby the classical turning points are located around $Z=3$–4 Å above the topmost surface atoms. Since a larger corrugation amplitude is observed for NiAl(110) compared to Cu(001), larger RID probabilities are also expected on the former surface. For comparison, we plot in Fig. 11 the same data shown in Fig. 10, but grouped together according to the corresponding RID transition. We see that in the energy range investigated, the normalized $0\rightarrow 2$ transition probability $Q(0,2)$ defined as $Q(i, j) = \sum_{m,n} R(mm:jj)$ is a factor of 2–3 larger than the $2\rightarrow 0$ one, in agreement with previous studies.

The data reported by Bertino et al. on Cu(001) were quantified using a definition of $R(mm:jj)$ slightly different from that of Eq. (4), in which the normalization was done considering the in-plane reflectivity of the sample. This means that the data of Fig. 11 must be multiplied by a factor of $\sim 3$ before being compared with the Cu(001) results. By doing this, we obtain that for an energy of about 100 meV, the $0\rightarrow 2$ and $2\rightarrow 0$ transition probabilities on NiAl(110) are about a factor of 2 higher than on Cu(001). So, this seems to confirm the expectation mentioned above of a correlation between larger corrugation amplitude (as seen in He atom scattering) with larger RID probabilities. However, there are several qualitative differences in the general behavior of the RID probabilities on these two surfaces. On Cu(001), for instance, the onset for the $1\rightarrow 3$ transition probability is around 100 meV, and both the $0\rightarrow 2$ and the $1\rightarrow 3$ transition probabilities increase by a factor of $\sim 10$ in the energy range studied. It is worth emphasizing that this onset is not due to a kinematic threshold since the rotational transitions observed were allowed in the energy range studied. Therefore, these differences point to the importance of the details of the corresponding PESs in the scattering process.

VII. CONCLUSIONS

We have measured rotationally inelastic diffractive scattering of $D_2$ from NiAl(110) at incident energies between 20 and 150 meV. The experiments were performed using a molecular beam, time-of-flight apparatus which combines high angular resolution with a high sensitivity. Several RID peaks were resolved in the in-plane angular distributions. The normalized scattering probabilities have been extracted from the experiment for a wide range of incidence energies. Furthermore, out-of-plane diffraction has also been measured in the same range of incident energies, providing a more complete data set than previously reported. The attenuation of the in-plane RID intensities with surface temperature was found to be in fair agreement with the Debye–Waller model. These results are expected to stimulate further theoretical studies, from which the role of the rotational degrees of freedom in the $H_2/D_2$ dissociation process could be finally understood.

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