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The role of the initial ro-vibrational state in molecule/surface scattering under fast grazing incidence

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Abstract. We have studied diffractive scattering of H_2 from LiF(100) under fast grazing incidence, as a function of the initial ro-vibrational state of the molecule. We show that diffraction patterns, i.e., the relative diffraction peaks intensity, vary significantly with the initial ro-vibrational state. This result indicates that in order to perform accurate comparisons between experimental and theoretical results, some knowledge about the initial ro-vibrational distribution of the molecular experimental beam is required. We hope that this result will encourage experimental groups working on the field to design and develop the techniques required to provide such information.

1. Introduction

Scattering of neutral diatomic molecules from surfaces under fast (200eV-25keV) grazing (1-3 deg.) incidence conditions received some attention during the early 90s [1, 2, 3]. But, it has been since the mid-2000s that this field has received a new impulse thanks to experiments showing molecular diffraction under these extreme conditions [4, 5]. The observation of diffraction under fast grazing incidence is possible due to the strong decoupling between the fast motion parallel to the surface along the incidence direction, and the slow motion perpendicular to it. Along the incidence direction the molecule feels a quasi-periodic potential, which means that along this direction the momentum change is almost zero. In the limit case, i.e., for a periodic potential (parallel incidence) the change of the parallel momentum along the incidence direction ($\Delta K_Y^{\parallel}$) is strictly zero, $\Delta K_Y^{\parallel} = -\frac{1}{\hbar v_Y} \int_0^d dY \frac{\partial V}{\partial Y} = \frac{1}{\hbar v_Y}[-V(X,d) + V(X,0)] = 0$ (see Ref. [6] for further details) -At this point it is worth emphasizing that the same mathematical result is obtained if one considers a constant potential along the incidence direction [7]. Therefore, any measurable momentum change of the molecule is due to a momentum transfer from the perpendicular motion to the motion parallel to the surface, and perpendicular to the incidence direction [6]. As the wavelength associated to the perpendicular motion (slow motion) is of the order of magnitude of the surface lattice constant, according to Bragg's diffraction law can be observed.

These experiments, which have been proposed as a very promising surface analytical tool to study, for example, surface properties and decoherence phenomena (see [8] and Ref. therein),

are rather challenging. Generating a high-energy neutral molecular beam is not an easy task. These kind of beams are generated in a three-steps process. First, high-energy ions are generated using a ECR (electron cyclotron resonance) based multicharge ions source, then these ions are mass and charge selected, and eventually the desired ions are neutralized in a gaseous charge exchange cell. So that, at the end of the process a well defined, in mass and energy, neutral beam is produced. However, this process does not allow to control, not even to estimate, the initial ro-vibrational state of the molecular beam.

First experimental results reporting diffraction of fast projectiles by surfaces under fast grazing incidences were performed in 2007 [4, 5]. First diffraction measurements using molecular projectiles were first carried out for H_2/NaCl(001) [5] and H_2/LiF(001) [4, 8]. Since then, experiments have been successfully performed for H_2 diffraction from more complex surfaces, such as ultrathin silica film on Mo(112) [9], superstructures of sulfur and oxygen atom on Fe(110) [10] or racemic alanine on Cu(110) [11]. On the other hand, the theoretical study of this type of phenomena presents a real challenge, mainly due to the high energy of the projectile, and the accuracy required for the six-dimensional (6D) potential energy surface (PES) describing the electronic structure of the molecule/surface system. However, some simulations have already been performed for low Miller-indices surfaces, by means of classical and semiclassical dynamics methods [12, 13, 14, 15].

These theoretical simulations, although based on simple classical dynamics, have already revealed a key issue to face when comparing theoretical and experimental results: the role of the internal degrees of freedom (DOFs) of the molecules. On the one hand, theoretical simulations carried out for H_2/Pd(111) and H_2/NiA/(110) have shown that a large proportion of the incoming molecules are rotationally excited upon scattering from the surface [12]. The rotational excitation shows up in the diffraction spectra, θ_f vs. ϕ_f (see Fig. 1a for angle definition) as a series of concentric circumferences, which results from the approximate energy conservation rule $\Delta k_Z^2/2M + \Delta E_{rot} \approx \Delta k_X^2/2M$, E_{rot} being the rotational excitation energy, M the mass of the projectile, Δk_Z the momentum change associated to the perpendicular direction to the surface, and Δk_X the momentum change associated to the motion parallel to the surface and perpendicular to the incidence direction. However, none of the few molecular spectra available in the literature display this arrangement of concentric circumferences of the diffraction peaks (only one broad cinrcumference is observed), which does not mean that experimental results can be used to conclude that molecular projectiles are not rotational excited upon scattering, it just means that rotational excitation cannot be resolved due to the limited experimental angular resolution. At the typical experimental conditions, for H_2/LiF(001), the polar angle spacing of these concentric circumferences associated, for example, with rotational excitations $H_2(J_i = 0 \rightarrow J_f = 2)$, $H_2(J_i = 1 \rightarrow J_f = 3)$ and $H_2(J_i = 0 \rightarrow J_f = 4)$ are about $0.07°$, $0.19°$ and $0.25°$, respectively, whereas the experimental angular resolution is about $0.5°$ (see Ref. [8]). On the other hand, the initial ro-vibrational state of the incident molecule may have a influence on the final diffraction spectra.

Here, we have investigated the influence of the initial ro-vibrational state of the molecules in the diffraction spectra using as benchmark system H_2/LiF(001), for which diffractograms data are available in the literature [16]. We show that direct and accurate comparisons between theory and experiment, similar to the ones perform usually at thermal or quasi-thermal energies [17], require the knowledge of the initial ro-vibrational distribution of the molecules.

2. Methodology
To perform our study we have worked within the Born-Oppenheimer static surface (BOSS) framework. Despite the fast motion of the projectiles in these experiments, the time scales associated to nuclei and electron motion are still different enough to trust in the validity of the Born-Oppenheimer approximation. On the other hand, the static surface approximation could
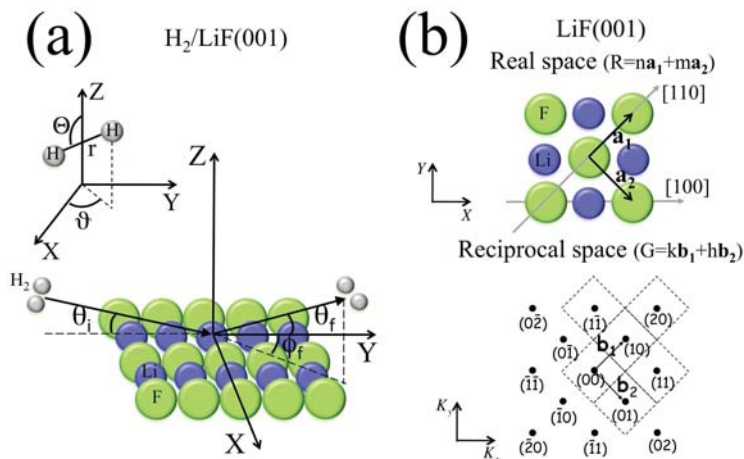
Figure 1. (a) The coordinate system used in the dynamics. The inset shows the DOFs included in the PES. (B) Real and reciprocal space for LiF(001). Dotted lines represent the Wigner-Seitz cell of the reciprocal lattice points.

be questioned, because the mass mismatch between the atoms of the molecule and the atoms of the surface is not that large. However phonons are not expected to play a crucial role. As already showed in experimental diffraction measurements at low incidence energy [18] phonons affect only the total diffraction intensity, but not the relative intensity of the peaks.

Working within the BOSS framework we have first computed the six-dimensional (6D) potential energy surface (PES) describing the electronic ground state of the system H_2/LiF(001) -the degrees of freedom (DOFs) considered in our study are shown in the inset of Fig. 1 (a). To compute the 6D PES ($V_{6D}(X,Y,Z,r,\Theta,\vartheta)$) we have applied the corrugation reducing procedure (CRP) [19] to a set of 4116 DFT (density functional theory) data. A detailed description of the 6D-PES is discussed elsewhere [20].

To perform our qualitative dynamics analysis of diffraction of H_2 from LiF(0001) under fast grazing incidence as a function of the initial ro-vibrational molecular state, we have taken a similar approach to that used in Ref. [21, 17] to study diffraction of thermal, or quasi-thermal, H_2 (and D_2) molecules from metal surfaces, and in Ref. [22] to study diffraction of fast H from LiF(001) under grazing incidence. Thus, we have taken use of a classical binning method to mimic diffraction probabilities. Briefly, using a classical binning method, the intensity of a given peak, (n,m), can be evaluated as the fraction of classical trajectories in which the molecules scatter with a parallel momentum change contained in the Wigner-Seitz cell of the (n,m) reciprocal lattice point (see Fig. 1 (b)) -see Ref. [23] for further details. The choice of this method to perform our analysis is based on previous results [21, 17, 22] showing that the *classical diffraction probabilities* mimic fairly well relative intensities of experimental spectra at thermal (or quasi-thermal) and high impact energies. At this point, it is worth pointing out that the method is expected to work better for fast projectiles, for which the change of parallel momentum (ΔK), respect to the total momentum, leading to diffraction is much lower -diffraction condition is given by $\Delta K = G$, G being a reciprocal lattice vector (see Fig. 1 (b)). On the other hand, in the case of alloys (with two or more atoms presented on the surface) the relative intensities of the diffraction peaks are modulated by the geometrical structure factor (see eq. 1), which might not be properly described by the classical binning method. However, for the experimental conditions we are considering here, the explicit comparison between classical and quantum results for diffraction of H_2 molecules on their ro-vibrational ground state ($J_i=0$, $v_i=0$) suggests that the classical binning method yields reasonable results. Thus, for the sake of computational cost, we have used this classical method to perform the required dynamics simulations as a function of the initial ro-vibrational state.
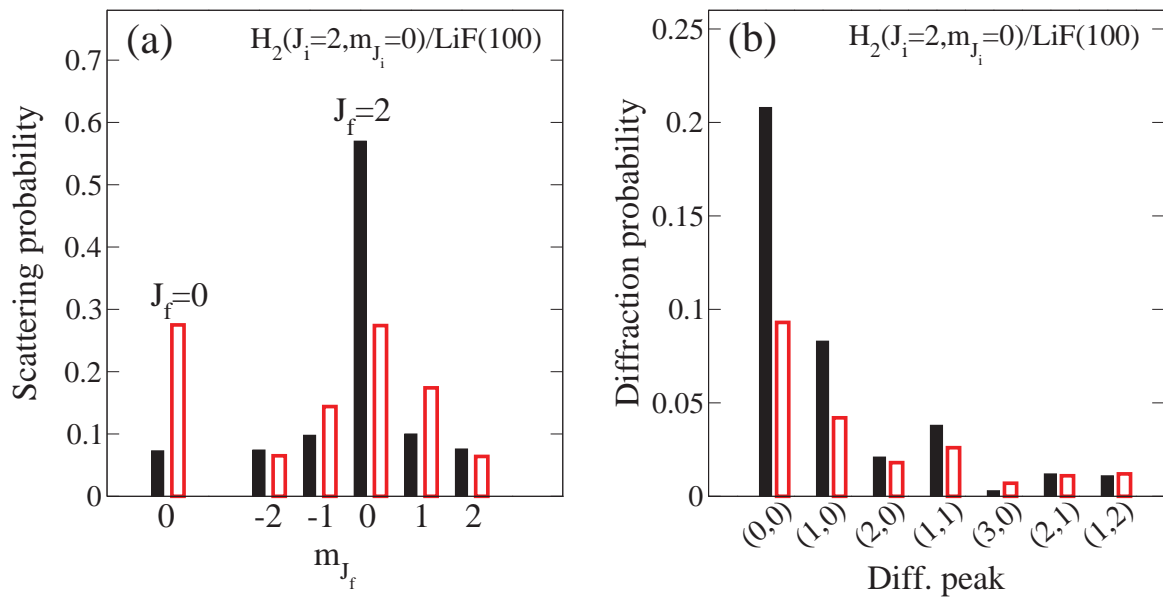
Figure 2.   (a) Rotationally (in)elastic scattering probabilities for $H_2(J_i=2,m_{Ji}=0) \rightarrow$ $H_2(J_f,m_{Jf})$. (b) Diffractionally (in)elastic scattering probabilities for $H_2(J_i=2,m_{Ji}=0) \rightarrow$ $H_2(J_f=2,\sum m_{Jf},(n,m))$. Solid bars: quantum results from Ref. [24]. Opened bars: classical results.

3. Results

First of all, in order to test the accuracy of our 6D PES and our classical dynamics method, we have performed some simulations at normal incidence and low incidence energy (E_i=100 meV), and we have compared our results with those obtained by Pijper and Kroes [24], using a 5D PES (the molecule was treated as a rigid rotor) and a quantum dynamics method [25]. At this point, it is worthy to point out that in order to ensure low statistical errors, we have run of the order of 10^5 trajectories for each classical simulation we discuss below. In Fig. 2 (a) we show the probabilities for classical and quantum rotationally (in)elastic scattering for the initial ro-vibrational state of the molecules (J_i=2,m_{Ji}=0). From this first comparison we can see that although classical calculations overestimate rotationally deexcitation and underestimate elastic scattering, they reproduce qualitatively the final distribution of the magnetic rotational quantum number, m_{Jf}. Furthermore, classical simulations yield a m_J change probability equal to 44%, close to the 35% found quantically. In Fig. 2 (b) we have compared quantum and classical results for diffraction peaks probabilities up to the 3rd diffraction order, for $H_2(J_i=2,m_{Ji}=0)$. Also in this case, the classical results reproduce qualitatively the quantum ones. Specifically, the relative intensities of the quantum diffraction peaks are qualitatively reproduced by our classical simulations. Therefore, from the qualitative agreement shown in Fig. 2, and taken into account that classical simulations are expected to work better at higher incidence energies as discussed above, we can conclude that our methodology is appropriate to perform the qualitative analysis we propose.

Although, we are proposing only a qualitative analysis, we take as references experimental results obtained by Rousseau et al [16]. In Fig. 3 we show the simulated diffraction spectra for incidence along two crystallographic directions $<100>$ and $<110>$ (see Fig. 1). In both cases, the normal energy is equal to 300 meV. At this point we should remind that diffraction spectra (number of peaks and peaks intensity) under fast grazing incidence only depend on the
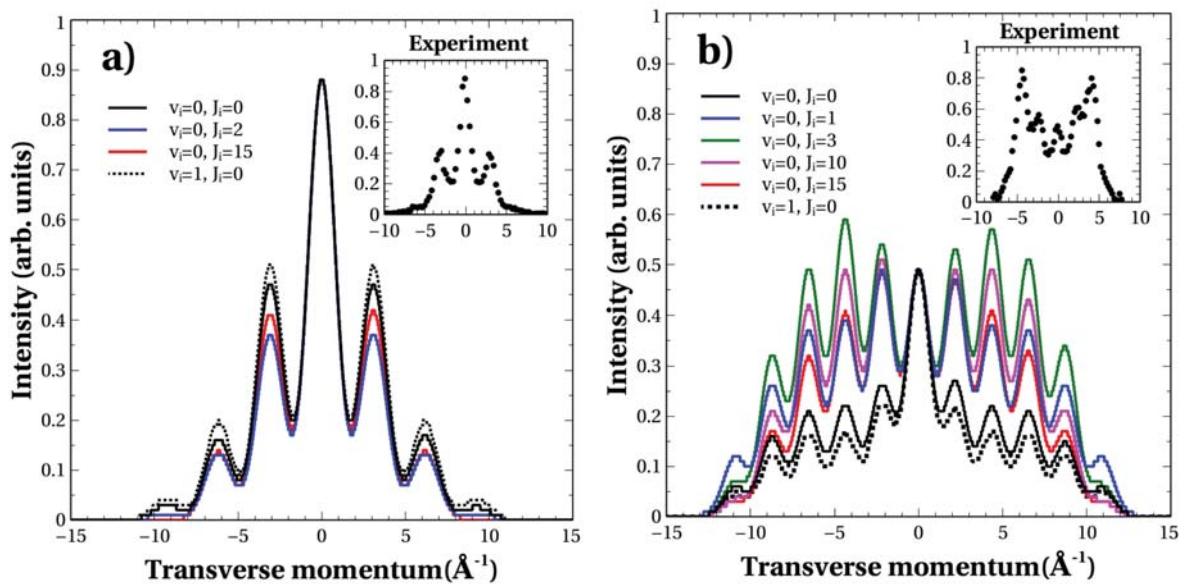
Figure 3. Diffraction spectra for H_2/LiF(001) simulated using classical dynamics, for several vibrational and rotational initial states. (a) Crystallographic direction $< 100 >$, and (b) Crystallographic direction $< 110 >$. Normal energy 300 meV . The insets show diffraction spectra recorded experimentally, data from Ref. [16]

normal energy -they are independent of the total energy and incidence angle. A first remarkable feature that can be extracted from this figure is that classical simulations capture pretty well the complexity of the H_2/LiF(100) PES. Simulations performed along the crystallographic incidence direction $< 110 >$ (Fig. 3 (b)) yield a higher number of diffraction peaks than along the $< 100 >$ one, because the corrugation is much higher along the $< 110 >$ direction than along the $< 100 >$ one, this result is in agreement with experimental results (see insets Fig. 3). Also in agreement with experimental results, we have found a stronger modulation of the diffraction intensity along the crystallographic direction $< 110 >$. In this direction, for example, the elastic peak is found to be less intense than the first and the second order ones; furthermore the second orderr peaks are the most intense ones. To understand this behavior we should remember that the amplitude of the diffraction peaks for polyatomic surfaces is modulated by the geometrical structure factor (S_G), which is given by:

$$S_G = f_{Li}(G)e^{i\mathbf{G}\mathbf{d}_{Li}} + f_F(G)e^{i\mathbf{G}\mathbf{d}_F}, \tag{1}$$

f_{Li} and f_F being the atomic form factors for Li and F ions, respectively. $\mathbf{d}_{Li}$ and $\mathbf{d}_F$ represent the atomic basis set vectors. The geometrical structure factor is equal to $f_{Li} + f_F$ if $n + m$ is an even number, and to $f_{Li} - f_F$ if $n + m$ is an odd number. Along $< 100 > n + m$ is always even, whereas along $< 110 > n + m$ is even and odd alternatively, which explains the stronger intensity modulation of diffraction peaks observed along this latter direction -for a more detailed discussion about the role of the S_G on diffraction from LiF(100) see Ref. [22].

A second remarkable feature that can be extracted from Fig. 3 is that the diffractive scattering patterns depend on the initial ro-vibrational state of the molecule. Overall, the agreement between theory and experiment seems to improve when higher rotational states are considered. Let us focus first on the crystallographic direction $< 100 >$, from Fig. 3 (a) we can see that increasing the rotational quantum number, J, decreases the intensity of the second and third order peaks, which are not observed experimentally (see inset Fig. 3 (a)). In fact, for $J = 15$

the third order peaks desapear. Thus, from Fig. 3 (a), we can see that the relative intensity of the diffraction peaks depends on the initial J value, and that theoretical results get closer to the experimetal ones when the initial J increases. If the initial vibrational state, v, increases the intensity of all the diffraction peaks increases. In this case no modulation respect to relative intensities obtained for $(v = 0, J = 0)$ is observed. In the case of the crystallographic direction $< 110 >$ the situation is more complex. For the initial ro-vibrational states $(v = 0/1, J = 0)$ theoretical simulations do not show the intensity modulation measured experimentally (see Fig.3 (b)). Contrary to experimental results, we have found that the specular peak is the more intense. However, when the initial J value increases, the intensity of the diffraction peaks increase with respect to the specular one. For $J = 3$, we recover the behavior observed experimentally, i.e., the second order peaks are the most intense ones. In Fig. 3 (b) we also show that the higher diffraction peaks obtained theoretically (but no measured experimentally) desapear for the highest initial J values. These results seem to indicate that an accurate comparison between experimental measurements and theoretical simulations will require some knowledge about the ro-vibrational distribution of the molecular experimental beam. Theoretical results should be weighted according to this initial ro-vibrational distribution. Thus, the probability of a given diffraction peak $I_{n,m}$ should be computed as:

$$I_{n,m} = \sum_{J,v} n(J,v) I_{n,m}(J,v). \tag{2}$$

$n(J,v)$ being the population of the ro-vibrational state (J,v) in the initial molecular beam.

4. Conclusions

In summary, we have performed classical dynamics simulations, using an accurate DFT-based six-dimensional potential energy surface, to evaluate diffractive scattering of H_2 from LiF(100). We have used quantum dynamics results at normal incidence and low incidence energy (E_i), and experimental results at fast grazing incidence, to validate our methodology. Eventually, we have studied the role of the internal degrees of freedom of the molecule in the diffraction process. We have shown that diffraction spectra may depend on the initial ro-vibrational state of the molecules, and therefore, an accurate comparison between theory and experiment will require some knowledge about the initial ro-vibrational distribution of the molecules beam. We hope that this study will stimulate experimental groups working on this topic to design and develop new experimental setups aiming to measure, or even to control, the initial ro-vibrational state distribution of the molecular projectiles.

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