In-Plane and Out-of-Plane Diffraction of H_2 from Metal Surfaces

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(Received 25 June 2004; published 8 December 2004)

We have measured in-plane and out-of-plane diffraction of H_2 and D_2 molecular beams scattered by reactive Pd(111) and nonreactive NiAl(110) surfaces at 140–150 meV. A comparison with six-dimensional quantum dynamics and classical trajectory calculations shows for the first time that accurate diffraction patterns can be obtained from state-of-the-art potential energy surfaces based on density functional theory. Our measurements show that, at general incidence conditions, out-of-plane diffraction is much more important than was assumed in previous experiments.

DOI: 10.1103/PhysRevLett.93.246104 PACS numbers: 68.49.Df, 68.43.–h, 82.65.+r

Studies of elementary collision processes of H_2 with metal surfaces can provide benchmark tests [1–3] of theoretical methods that are increasingly used to aid in the design of new heterogeneous catalysts [4]. Molecular beam and associative desorption experiments have been carried out to understand the main factors that govern H_2 dissociation at the surface [5–7]. In addition, vibrationally inelastic [8,9] and rotationally inelastic [10] scattering experiments, complemented by theoretical research [11,12], have provided useful information on how certain features of the potential energy surface (PES) control the experimental observations [13].

A different point of view is provided by diffraction experiments. As is well known, He-atom scattering is a common tool to investigate surface properties [14]. 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, i.e., the PES. The situation is already much more complex with a molecule as simple as H_2, even though its stronger interaction with the surface makes diffraction intensities larger than for He. This is because the multidimensional character of the H_2-surface problem comes into play and, in particular, the coupling with the dissociative adsorption channels. Thus, H_2 diffraction has been proposed some time ago as a promising (and maybe unique) experimental technique to gauge the molecule-surface PES and dynamics [15,16]. Accordingly, the eikonal approximation (based on a hard corrugated wall potential [14]), which has been the basis for the interpretation of most He experiments, is *a priori* of much less value for the case of molecules. Therefore it seems appropriate to check the validity of state-of-the-art PESs, such as those obtained from *ab initio* density functional theory (DFT), together with full dimensional dynamics. Such a confrontation between theory and experiment has not been achieved so far. It is the aim of the present work to show its practicability, the conditions for its successful completion, and the first conclusions that can be reached.

Although evaluation of DFT PESs for H_2/metal surface systems is not trivial and 6D quantum dynamical (QD) calculations, which treat all six H_2 degrees of freedom, are computationally demanding, an exact theoretical description of H_2 scattering from first principles (within the rigid surface model and Born-Oppenheimer approximations) is now possible [17,18]. So far only a few predictive 6D QD studies of diffraction have been carried out: H_2/Pd(100) [19], H_2/Pt(111) [20], and HD/Pt(111) [21] (all reactive systems). An important prediction of these studies is that out-of-plane diffraction can be as important as [19] or more important than [20,21] in-plane diffraction. It is at this point that the main experimental limitations appear: to check the validity of the PES, the experimental setup must allow for both in-plane and out-of-plane measurements with high enough resolution to deal with reflectivities that are of the order of a few percent [13,22]. Only a few experimental attempts have been able to meet these demands [22,23].

Up to now, such experiments have not provided evidence for the prediction that out-of-plane diffraction can dominate under general incidence conditions [19,20]. On the other hand, measurements reported in [22] suggest that, for the reactive H_2/Pd(111) system, out-of-plane diffraction dominates in-plane diffraction under special incidence conditions: large incidence angles. This observation has been qualitatively explained as resulting from the periodic potential seen by a classical particle traveling parallel to the surface [22] and from limitations in energy transfer [20], but these explanations say nothing about the important characteristics of the PES. This is relevant because the relative height of diffraction peaks strongly depends on the PES shape, which differs significantly from one system to the other, even in the approach toward the surface where it may be anything between strongly attractive (as in many nonactivated systems) and strongly repulsive (activated systems with early barriers). In this Letter, we present a comparison between theory and experiment for H_2 diffraction from the highly reactive Pd(111) and less reactive NiAl(110) surfaces.

The H_2/D_2-diffraction experiments were performed with the apparatus described in detail in Ref. [24]. Briefly, it consists of a three-stage differentially pumped beam system and an 18 in. diameter UHV scattering chamber. The free jet expansion is produced through a nozzle of $d = 10\ \mu$m diameter. The nozzle temperature T_0 can be varied between 300 and 700 K, allowing a variation of the H_2 (D_2) incident energy between 75 and 160 meV. The measurements reported here were performed with a source pressure $P_0 = 30$ bar behind the nozzle. The velocity spread of the H_2/D_2 beams was estimated to be 8% under these conditions, as judged from the angular resolution observed in the H_2/D_2-diffraction spectra as compared to He-diffraction data. The base pressure in the chamber was typically $\sim 3 \times 10^{-10}$ mbar, reaching $\sim 8 \times 10^{-10}$ mbar with the H_2/D_2 beams on. The angular distribution of the scattered molecules was analyzed with a quadrupole mass spectrometer mounted on a two-axis goniometer. This arrangement allows rotations of 200° in the scattering plane (defined by the beam direction and the normal to the surface) as well as ±15° from the scattering plane for a fixed angle of incidence.

Figure 1 shows sphere models of the Pd(111) and NiAl(110) surfaces and the corresponding reciprocal lattices. Both surfaces were prepared in UHV by several cycles of sputtering with Ar^+ ions and heating. Further details on Pd(111) [25] and NiAl(110) [26] sample preparation can be found elsewhere. During the measurements on Pd(111), the crystal temperature was kept at 430 K, i.e., well above the H$_2$/Pd desorption temperature of $\sim$350 K [27], to prevent the buildup of an adsorbed layer of hydrogen. NiAl forms an ordered alloy in a CsCl structure while its (110) surface is terminated by 50% Ni and 50% Al atoms. Hydrogen dissociation is activated on this system: the minimum barrier for dissociation has been estimated to be 0.3 eV [28]. Therefore, measurements on NiAl(110) were performed with the crystal at 90 K. The rotational populations of the incident H_2/D_2 beams in our experiment were estimated from previous theoretical and experimental work [29]. For an incident energy $E_i = 150$ meV, most H_2 molecules are in the $J_i = 1$ state (60%), while 38% of D_2 molecules are in the $J_i = 2$, 18% in the $J_i = 1$, and 16% in the $J_i = 0$ state. Because of the large spacing between the vibrational levels of the H_2 molecule, more than 99% of the molecules are in the $v_i = 0$ state for $E_i \leq 200$ meV.

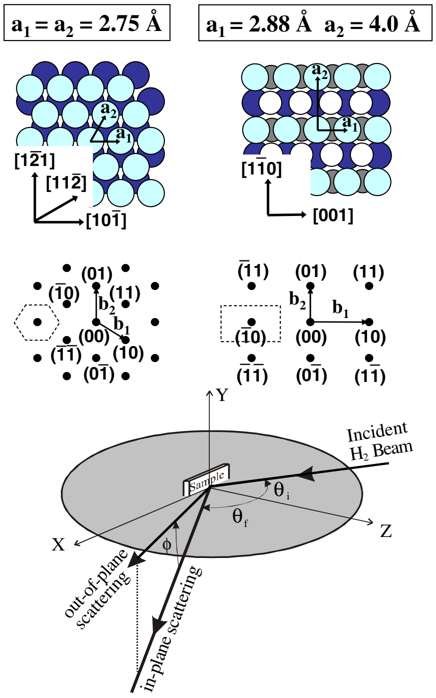

FIG. 1 (color online). Sphere models of the Pd(111) and NiAl(110) surfaces. The primitive unit cells, the corresponding reciprocal lattices, and the experimental scattering geometry are also shown.

The theoretical methods used in this work have been described in detail earlier [30,31]. Briefly, we use the PESs of [28,32] for H_2/Pd(111) and H_2/NiAl(110), respectively, determined by application of the corrugation reducing procedure [33] to *ab initio* DFT calculations. This procedure has been shown to provide a precision better than 30 meV in several systems [28,32,34]. For H_2/Pd(111), we have used the calculated PES to perform quantum dynamics calculations using a time dependent wave packet method [20]. The method uses a discrete variable/finite basis representation for all degrees of freedom. The initial wave packet is propagated in time using the split-operator method. The reflected wave packet is analyzed using a scattering amplitude formalism. For both systems, we have also performed classical trajectory calculations in which the initial vibrational zero point energy (ZPE) of H_2 or D_2 is not included (see [30] for details). We have shown [30] that exclusion of the ZPE leads to slightly smaller dissociation probabilities, but it barely affects (i) the angular distribution of reflected molecules and (ii) the variation of the dissociation probability with incidence angle. The method is equivalent to performing "classical molecular dynamics calculations" using *ab initio* PESs but restricted to the H_2 degrees of freedom (surface atoms are fixed). In this context, the probability of a given (n, m) diffraction transition is evaluated as the fraction of trajectories in which the molecule scatters nonreactively with a parallel momentum change contained in the 2D Wigner-Seitz cell built around the (n, m) lattice point in reciprocal space (see dashed polygons in Fig. 1 and [35] for details). To take into account the rotational excitation of the H_2/D_2 beams used in the experiments, we have performed classical trajectory calculations for initial angular momenta $J_i = 0$–3 in the case of $H_2/Pd(111)$, and $J_i = 0$–4 in the case of $D_2/NiAl(110)$. Quantum calculations have been restricted to the dominant $J_i = 0, 1$ initial states. The initial population of the different rotational states has been taken from experiment. The comparison between theory and experiment is done assuming that the ratios of experimental diffraction peak intensities are equal to the ratios of calculated diffraction probabilities, i.e., equal Debye-Waller attenuation for all diffractive transitions.

Experimentally, diffraction probabilities are extracted from the peak intensities observed in the angular distributions (in θ_f) of molecules scattered in the plane of incidence and other planes (see Fig. 1 and Refs. [13,14]). Figure 2 shows such diffraction spectra, as recorded along the $[10\bar{1}]$ azimuth of Pd(111). The incidence angle θ_i, measured with respect to the surface normal, is 52° and the incident energy 140 meV. To allow a better comparison with theory, the spectra are presented after background substraction. This background is mainly due to phonon inelastic scattering, which is not taken into account in the theoretical calculations. We have estimated that the reflectivity at 430 K associated with the (00) and symmetry related (01) and $(0\bar{1})$ elastic peaks (defined as the ratio between measured diffraction peaks and incident beam intensity) is 0.5%, which is lower than the value obtained in our quantum calculations, 2.8%. This difference is again due to inelastic phonon scattering not included in the theory (a Debye-Waller extrapolation [13] of the experimental value to 0 K leads to 3%, in excellent agreement with the theoretical value). The calculated total reflectivity is 12.5%. The difference between the latter value and that corresponding to the (00) + (01) + $(0\bar{1})$ directions is mainly due to the less intense but many out-of-plane peaks appearing at $\phi_f > 15°$ (i.e., outside the angular range covered in the present experiment).

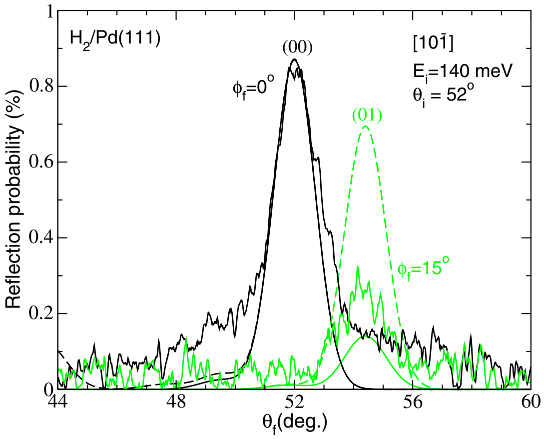

FIG. 2 (color online). In-plane ($\phi_f = 0°$) and out-of-plane ($\phi_f = 15°$) H_2 diffraction spectra for Pd(111). Black curves: in-plane diffraction; green curves: out-of-plane diffraction. Solid lines: experiment; smooth solid curves: 6D quantum dynamical calculations; smooth dashed curves: 6D classical trajectory simulations. Theoretical results have been convoluted with a Gaussian function of width $\sigma = 0.7°$ (the angular resolution of the measurements). Both experimental and classical trajectory results have been normalized to the specular peak that arises from quantum calculations. θ_f is the angle between the direction of observation and the surface normal, and ϕ_f is the reflection angle referred to the incidence plane, as defined in Fig. 1. The surface temperature is 430 K.

A remarkable feature of these spectra is the appearance of pronounced out-of-plane diffraction, while no diffraction peaks are observed in the scattering plane. Figure 2 shows an excellent agreement between the experimental and the quantum dynamical results, showing that the PES used is accurate enough for describing diffraction. The intensity of the (01) peak obtained from the classical trajectory calculations is overestimated. However, this is the only diffraction peak predicted by the latter calculations: for all other peaks allowed by the Bragg law (34 peaks) but not seen in the experiment, classical trajectory results predict a very low intensity, in excellent agreement with quantum calculations. We have found similar results for 50° and 150 meV. This suggests that the dominant patterns can be correctly predicted by classical trajectory calculations using a DFT PES.

Figure 3 shows D_2-diffraction spectra measured along the $[1\bar{1}0]$ azimuth of NiAl(110) at an incident energy of 150 meV and an incidence angle of 23.5°. In this case, the experimental data are only compared with classical trajectory calculations because the latter are much cheaper than quantum calculations and, as shown for the Pd(111) case, lead to a correct physical description of diffraction. It is remarkable that classical trajectory calculations predict the appearance of both in-plane and out-of-plane diffraction peaks, in agreement with experiment.

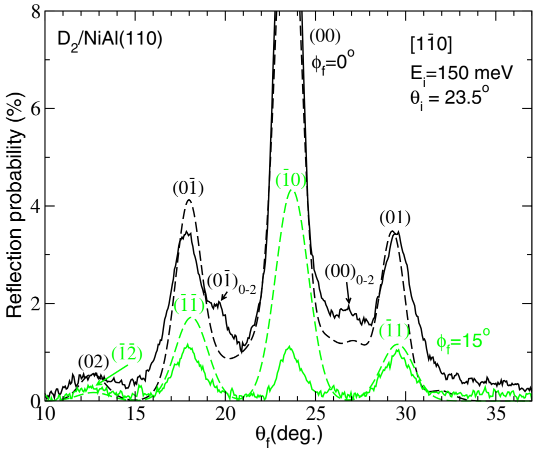

FIG. 3 (color online). In-plane ($\phi_f = 0°$) and out-of-plane ($\phi_f = 15°$) D_2 diffraction spectra for NiAl(110). The surface temperature is 90 K. Same notations and conventions as in Fig. 2, except no 6D quantum calculations are presented. The experimental results were normalized to the (01) in-plane peak obtained from the classical dynamics calculations. Rotationally inelastic diffraction peaks are denoted by their Miller indices (n, m) and a subscript indicating the rotational transition $J_i \rightarrow J_f$.

Although the out-of-plane $(\bar{1}0)$ peak is overestimated, and the specular peak is underestimated by ~25%, the relative intensities of all other diffraction peaks are well reproduced by the classical trajectory calculations. Once again, peaks allowed by the Bragg condition (77 peaks) but not observed in the experiment are not obtained in the classical trajectory calculations either. We have found similar results for incidence angles of 33° and 40°. Therefore, we feel confident in using classical trajectory calculations to interpret our experimental results.

The experimental results show that, for general incidence conditions, out-of-plane diffraction is more important than previously assumed in H_2 diffraction experiments [13,14], particularly for H_2/Pd(111) where it swamps in-plane diffraction. Our classical trajectory calculations show that most molecules are reflected relatively far from the surface: $\simeq 3$ and $\simeq 1.5$ Å above the topmost surface atoms of NiAl(110) and Pd(111), respectively. In the D_2/NiAl(110) case, the PES is strongly repulsive in the incidence channel, which explains why D_2 molecules are reflected farther than in H_2/Pd(111) and why diffraction is relatively small compared to specular reflection. In the H_2/Pd(111) case, the potential is attractive and molecules approach, on average, closer to the surface (though always above $\simeq 1.5$ Å since those approaching closer dissociate). Consequently, reflected molecules feel a stronger corrugation and, therefore, diffraction is relatively more important compared to specular reflection. Our classical trajectory calculations show only a similar suppression of the specular peak in D_2/NiAl(110) at much higher impact energies.

In conclusion, the present comparison between theory and experiment suggests that quantum (classical) dynamics calculations based on DFT potentials and treating all molecular degrees of freedom can accurately (semiquantitatively) predict diffraction patterns for H_2 scattering from reactive as well as nonreactive metal surfaces. The importance of out-of-plane diffraction demonstrated by our experiments for general incidence conditions shows that its measurement is crucial to test the quality of any PES.

This work was supported by the DGI (BFM2003-00194, BQU2001-0147), the CAM (07N/0041/2002), and the grants "Ramón y Cajal," FPU, and CW. We thank the CCC-UAM and NCF for computer time and K. H. Rieder for the donation of the diffraction apparatus.

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