Reactive scattering of H₂ from metal surfaces under fast-grazing-incidence conditions

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We have studied the interaction of molecular hydrogen with metal surfaces under fast-grazing-incidence conditions, by means of classical dynamics calculations based on density functional theory six-dimensional potential energy surfaces. We have performed calculations on two activated systems, $H_2/NiAl(110)$ and $H_2/Cu(111)$, and on two nonactivated systems, $H_2/Pd(111)$ and $H_2/Pd(110)$. We show that for rather open surfaces the computed 1 - R probabilities (where *R* represents the reflectivity) as a function of the normal collision energy at grazing incidence (along low-Miller-index directions) mimic reasonably well the dissociative adsorption probabilities obtained at normal incidence and thermal energies from the dissociation threshold up to the saturation limit. Our results indicate that fast grazing incidence experiments could be used as complement to traditional sticking experiments at thermal energies to determine dissociative adsorption saturation limits, which are usually unreachable due to limitations in traditional molecular beam experiments

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I. INTRODUCTION

The interaction of fast atoms and molecules with surfaces (metal, semiconductor, and insulator surfaces) under grazingor nearly-grazing-incidence conditions was extensively investigated, both theoretically and experimentally, in the 1990s [1-14], due to its potential use as analyzing tool in diverse fields such as heterogeneous catalysis, environmental chemistry, or material modification. The vast majority of the experiments were focused on scattering of ionic projectiles, which are technically easier to generate than neutral ones. Thus, for example, scattering of fast Ne⁺ and He⁺ were used to study structural changes of the Pb(110) surface [7]. Experiments using also Ne⁺ projectiles were performed to study inelastic energy loss in scattering of ions from a Si surface [11]. From a theoretical point of view, model potential energy surfaces and classical methods have been recently developed and employed to study scattering at grazing incidence of He⁺, Ne⁺, and Ar⁺ from Pt(111)-(1×1) [15] and Si(100) [16]. Scattering of molecular ionic beams $(H_2^+ \text{ and } D_2^+)$ has also been studied, both theoretically and experimentally. For example, dissociative scattering has been studied for H₂⁺ interacting with Ni surfaces at grazing incidence [1,2], showing that the dissociation of the projectile is mainly due to electronic processes and not to a direct process. The energy distribution of scattered H atoms on grazing scattering of H_2^+ from Pt(110) and Ag(110) was used to obtain information about the molecule during the scattering process after electron capture [14]. In the case of D_2^+ , experiments on molecular dissociation upon scattering from Ni have been performed recently [17].

Experiments on scattering of neutral projectiles under grazing incidence are more challenging, because, in this case, the primary ionic beam must first neutralized (usually using a charge-exchange cell). This kind of experiments has been performed, for example, by Souda *et al.* [10], who used scattering of fast (0.1–2 keV) Ne atoms from Si(001), Al(111), and polycrystalline Mg surfaces to study collision-induced electronic excitation. Experiments using neutral molecular projectiles were carried out by van Slooten *et al.* [5] on $H_2/Ag(111)$. These authors also performed classical dynamics calculations [5,6,8] showing, for example, an important energy transfer from translational to rotational motion, as well as the importance of the initial orientation of the molecule on the dissociation.

In the past few years, this topic has received a new interest thanks to experiments showing diffraction of fast (0.2–2.5 keV) light projectiles scattered at grazing incidence (1–3 degrees) from clean alkali-metal halide [18–20], metal [21,22], and superstructures adsorbed on metal surfaces [23]. Diffraction of light atoms and molecules was already observed in the 1930s [24]. But it was believed for long time that it was not possible to observe diffraction at such high energies, because for these incidence energies the associated de Broglie wavelengths are much smaller than the typical surface lattice constant and, therefore, comparable to the typical thermal displacements of the surface atoms, which introduces decoherence hiding diffraction [25]. Another phenomenon that, in principle, could introduce decoherence is surface electronic excitations. Electronic excitations lead to energy dissipation and therefore to decoherence [26]. However, electronic excitations have been proved to be negligible in wide band-gap insulators [13], as well as in metal surfaces [21]. This later statement is supported by experimental measurements showing atom diffraction from metal surfaces [21-23].

These experimental findings open new possibilities to develop novel tools in fields as diverse as structural and dynamical properties of surfaces, decoherence phenomena in quantum scattering, or atomic optics. And they have also driven the development of new theoretical studies. The mechanism that explains the physical phenomenon behind these experimental observations was recently proposed by Farías *et al.*

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FIG. 1. Schematic representation of a grazing incidence collision of H_2 with a metal surface. The coordinate system used in the dynamics is also shown.

[27], who used it to explain the predominance of out-of-plane diffraction in the diffraction pattern of H_2 scattered from Pd(111) [28] at thermal energies and low incidence angles (with respect to the surface). When a molecule moves along a periodic direction, the momentum change along this direction (hereafter called parallel longitudinal direction) is zero because any acceleration is compensated with a slowing down, i.e.,

$$\Delta k_{\parallel} = -\frac{1}{\hbar v_Y} \int_0^d dY \frac{\partial V}{\partial Y} = \frac{1}{\hbar v_Y} [-V(X,d) + V(X,0)] = 0,$$
(1)

 Δk_{\parallel} being the parallel logitudinal momentum change, v_Y the molecule velocity, in this case for incidence along the *Y* axis (see Fig. 1), and *d* the distance over which the potential V(X,Y) replicates. Therefore any change in the momentum of the projectile comes from the momentum transfer from the motion normal to the surface to the motion parallel to the surface and perpendicular to the incidence direction (hereafter called parallel transverse direction), because

$$\Delta k_{\perp} = -\frac{1}{\hbar v_Y} \int_0^d dY \frac{\partial V}{\partial X} \neq 0, \qquad (2)$$

where Δk_{\perp} represents the parallel transverse momentum change.

In the case of fast grazing incidence the motion normal to the surface is very slow, and, therefore, its associated de Broglie wavelength is comparable to the surface lattice constant. Thus, according to Bragg's law, when the transverse momentum transfer coincides with a reciprocal lattice vector out-of-plane diffraction is observed [19,29].

In spite of the large number of diffraction experiments, to our knowledge, no experiment has ever reported dissociative adsorption or total reflectivity probabilities under fast grazing incidence conditions.

From a theoretical point of view, most studies on grazing incidence have focused on scattering of fast atoms from alkalimetal halide surfaces (see, for example, Refs. [30–32]). In a recent work [29] we have shown that molecular dissociative adsorption probabilities for low incidence energies can be obtained from total reflectivity probabilities resulting from fast grazing incidence. Dissociative adsorption of molecules on metal surfaces at thermal energies has been widely studied, both theoretically and experimentally (see, e.g., Refs. [33–36] and reference therein). However, technological limitations associated with experimental setups at thermal energies restrict

these experiments to very low incidence energies (typically lower than 1.0 eV for light molecules [37,38]). The energy reached by these experiments is usually below the energy needed for saturation, which means that the dissociative adsorption saturation values have to be extrapolated from the available data at low incidence energies. This latter procedure frequently leads to wrong results (see, for example, Ref. [39]). Thus, experiments at fast grazing incidence will open a unique possibility to measure saturation values at thermal energies, considering that, in this kind of experiment, the interaction between the molecule and the surface is governed almost exclusively by the normal energy [19,27,29], which is of the order of few hundreds of meV's.

In the present article we analyze the conditions under which grazing incidence experiments could be used to mimic dissociative adsorption at thermal energy. To perform our analysis we have chosen four systems, two activated systems, H₂/NiAl(110) and H₂/Cu(111), systems that present a minimum reaction barrier, and two nonactivated systems, H₂/Pd(111) and H₂/Pd(110), systems that present reaction paths without a reaction barrier. These four systems have been well studied at low incidence energy and normal incidence conditions, see Refs. [38,39] for H₂/NiAl(110), Refs. [40–43] for H₂/Cu(111), Refs. [44–46] for H₂/Pd(111), and Refs. [47,48] for H₂Pd(110).

The article is organized as follows. In Sec. II, we briefly outline the theoretical methods used in this work. In Sec. III we discuss the dynamics results obtained for these four systems. Finally, we summarize the main conclusions in Sec. IV.

II. THEORETICAL APPROACH

Theoretical methods used to perform this study have been described in detail elsewhere, so only a brief summary is given here. The six-dimensional (6D) potential energy surfaces (PESs), describing the electronic interaction between the molecule and the surface for the four systems investigated here, were computed by applying the corrugation reducing procedure (CRP) [49] to a set of density functional theory and generalized gradient approximation (DFT-GGA) data. These PESs have been used previously to study the four systems investigated here at slow normal incidence [39,42,43,46,48,50,51]. For specific details of the PESs see Ref. [52] for H₂/NiAl(110), Ref. [46] for H₂/Pd(111), Ref. [48] for H₂/Pd(110), and Ref. [53] for H₂/Cu(111).

The dynamics calculations have been carried out by using classical and quasiclassical methods [54]. Within the classical dynamics framework, a trajectory is computed by solving the Hamilton equations of motion, and the reflection probability for each collision energy (E_i) and rovibrational state (v, J) is calculated as an average over the molecular initial internal coordinates and internal conjugated momenta, which are obtained by using a classical Monte Carlo sampling method. We have employed both the classical (C) and the quasiclassical (QC) approach (for a detailed discussion about these two approaches see, for instance, Ref. [46]). The C approach, which does not include the zero-point energy (ZPE) of the molecule, has been shown to give good results for nonactivated systems. This is the reason why we have used this approach to study H₂/Pd(111) and H₂/Pd(110). In contrast, the QC

approach, which includes the ZPE, gives in general accurate results for activated systems (see Ref. [36] and references therein), such as H₂/NiAl(110) and H₂/Cu(111). In order to obtain low statistical errors we have computed of the order of 2×10^4 trajectories for each set of initial conditions (E_i, v, J). At the end of the trajectory the molecule is considered to be reflected whenever the molecule-surface distance Z (see Fig. 1) becomes equal to Z_i (initial distance molecule-surface) with the molecule's velocity vector pointing toward the vacuum.

III. RESULTS

We have studied grazing incidence scattering of H_2 and D_2 from clean Cu(111), Pd(111), and Pd(110) surfaces and the alloy NiAl(110) metal surface. $H_2/Pd(111)$ and $H_2(Pd(110)$ are nonactivated systems, whereas $H_2/Cu(111)$ and $H_2/NiAl(111)$ are activated systems.

A. Activated systems

For activated systems, such as H₂/NiAl(110) and H₂/Cu(111), at low energy (<2 eV) and normal incidence the dissociative adsorption curves as a function of the collision energy present a typical **S** shape [55]. The dissociative adsorption probability increases monotonically from the energy threshold, which is approximately given by the minimum reaction barrier height, to the saturation value. In Fig. 2 we show that the complementary to total 1 - R as a function of the normal energy (E_n) of H₂ molecules scattered from NiAl(110) at grazing incidence also shows this S-shape behavior. In Fig. 2(a) we show 1 - R as a function of the



FIG. 2. (Color online) 1 - R as a function of the normal incidence energy for (A) $H_2(v = 0, J = 0)/NiAl(110)$, at normal incidence and at fast grazing incidence along the crystallographic direction [001] for several total energies (E_i) between 0.2 and 2.0 keV; (B) $H_2(v = 0, J = 0)/NiAl(110)$, at normal incidence and at fast grazing incidence along several crystallographic directions for $E_i =$ 400 eV. Quasiclassical calculations.

normal incidence energy for molecules striking the surface along the crystallographic direction [001] with several total collision energies (E_i) from 0.2 to 2.0 keV. In order to cover the whole normal energy range shown in Fig. 2(a) (0.25–2.0 eV), for each total energy we have changed the incidence angle θ_i within a range $[\theta_i^{\min} - \theta_i^{\max}]$. For $E_i = 200$ eV, θ_i lies in the interval [2.03°–5.74°], for $E_i = 400$ eV in the interval $[1.43^{\circ}-4.06^{\circ}]$, for $E_i = 800$ eV in $[1.01^{\circ}-2.87^{\circ}]$, and for $E_i = 2 \text{ keV in } [0.64^\circ - 1.81^\circ]$. Figure 2(a) shows that the 1 - Rcurves obtained under fast grazing incidence conditions mimic almost perfectly the dissociative adsorption curve obtained for low energy at normal incidence [38,39]. From Fig. 2(a) we also see that this conclusion does not depend on the total energy. This finding supports the hypothesis that the interaction between a fast projectile under grazing incidence and a surface is mainly governed by the molecular motion normal to the surface.

At that point, some comments are appropriate. At low energies (below 2.0 eV) the majority of the H₂ molecules interacting with metal surfaces either scatter or dissociate on the surface. Consequently, dissociative adsorption can be considered as the complementary phenomenon to molecular reflection, i.e., dissociative adsorption probabilities can be computed (or measured) as 1 - R. However, strictly speaking, dissociative adsorption is not possible under fast-grazingincidence conditions due to the high parallel energy of the molecule. Our calculations show that the H atoms resulting from H₂ dissociation do not remain bound to the surface, but they are *randomly* scattered from it. In spite of this, Fig. 2 clearly shows that the 1 - R probability obtained at grazing incidence behaves exactly as the dissociative adsorption probability at thermal energy.

From Fig. 2(b) we can see that the quality of the agreement between grazing and normal incidence results depend on the crystallographic direction, i.e., on φ (see Fig. 1). In this figure we have plotted 1 - R as a function of the normal energy for serveral incidence directions (φ), including the low-Millerindex crystallographic directions [001], [110], and [111], for $E_i = 400$ eV. Generally speaking, the agreement is better when the molecule moves along a symmetry direction with low Miller indices. Under these grazing incidence conditions, the collision proceeds in channeling regime [56], where the rows formed by the surface atoms guide the projectile in its motion along the surface. The channeling is expected to be better for wide channels than for narrow channels, because the narrower the channel the larger the probability for the projectile to hit the repulsive zones of the PES (the potential walls) and be scattered. In the case of NiAl(110), the widest channels are found along the [001] direction, which explains why the best agreement is obtained for incidence along this direction. It should be noted that throughout this article the width of the channel is defined as the distance between two neighbor atoms in the direction perpendicular to the incidence direction projected on the surface. For NiAl(110), the width of the widest channel is 4.08 Å [52] (along the [001] direction), whereas it is 2.89 Å [52] along the [110] direction. In our definition of channels for NiAl(110), we have only taken into account Ni atoms. Al atoms are not considered because the electronic density around these atoms is much smaller than the electronic density around Ni atoms, as shown in Fig. 3,



FIG. 3. (Color online) Three-dimensional representation of the electronic density distribution over the NiAl(110) unit cell at several distances (Z) over the surface.

where we have plotted the electronic density distribution over the NiAl(110) unit cell.

The role played by the width of the channel is corroborated by results obtained for another activated system H₂/Cu(111) [see Fig. 4(a)]. The widest channel in Cu(111) is 2.62 Å [53] (along the incidence direction [101]), which is about half of the widest channel in NiAl(110). Thus, the calculated 1 - R probabilities under fast grazing incidence along the [101] direction does not reproduce the 1 - R curve at normal incidence as accurately as for NiAl(110). Similarly to H₂/NiAl(110) the 1 - R results do not depend on the total energy [see Fig. 4(a)]. Figure 4(b) shows results obtained for H₂ colliding with Cu(111) along several incidence directions (φ), including the low-Miller-index crystallographic directions [101] and [121], for $E_i = 400 \,\text{eV}$. As can be seen, the agreement becomes worse when the molecule moves along crystallographic directions associated with narrow channels.

The 1 - R (or dissociative adsorption) results presented above have been obtained for H₂ molecules initially in its ground rovibrational state (v = 0, J = 0). But, the experimental setups used to produce molecular beams at fast grazing incidence [13,18] do not guarantee a significant population of the molecular ground state in the beams, on the contrary, high rotational and vibrational states are expected. Therefore, we have analyzed whether the agreement obtained for $H_2(v = 0, J = 0)$ remains when we deal with vibrationally and rotationally excited molecules. In Fig. 5 we show 1 - Rresults for several initial rotational and vibrational states. In the case of NiAl(110), dissociative adsorption (1 - R)probabilities for rotationally excited molecules at low energy and normal incidence are very well reproduced under grazing incidence [see Fig. 5(b)]. For vibrationally excited molecules, dissociative adsorption probabilities are also reasonably well reproduced by grazing incidence calculations, but, in this case, the agreement is slightly worse when v increases [see Fig. 5(a)]. The same behavior is observed for $H_2/Cu(111)$



FIG. 4. (Color online) 1 - R as a function of the normal incidence energy for (A) $H_2(v = 0, J = 0)/Cu(111)$, at normal incidence and at fast grazing incidence along the crystallographic direction [101] for several total energies between 0.2 and 2.0 keV; (B) $H_2(v = 0, J = 0)/Cu(111)$, at normal incidence and at fast grazing incidence along several crystallographic directions, for $E_i = 400$ eV. Quasiclassical calculations.

[see Figs. 5(c) and 5(d)], although, for this system, as discussed above, the results are not as good as for H₂/NiAl(110).

We have also studied the effect of replacing H_2 by D_2 . As can be seen in Fig. 6, no appreciable isotopomer effects have been found.

B. Nonactivated systems

It could be thought that the good agreement obtained in the case of activated systems may be mainly due to the fact that both reflection and dissociative adsorption are direct processes, i.e., the molecule approaches the surface and then it is reflected or dissociates, but without exploring too much the surface. However, nonactivated systems behave differently at thermal energies. In these latter systems the molecule can explore the surface through the so-called dynamics trapping. A dynamically trapped molecule rebounds several times on the surface until it gets dissociative adsorbed or is reflected. This trapping mechanism allows the molecule to explore the surface. As discussed in Ref. [46] the nonmonotonic behavior found for dissociative adsorption (and reflectivity) in nonactivated systems, at normal incidence and thermal energy, is due to dynamic trapping. Now the question is: Could molecular scattering under fast-grazing-incidence conditions reproduce molecular scattering at thermal energy and normal incidence for nonactivated systems? To answer this question we have studied fast grazing incidence scattering of H₂ from Pd(111) and Pd(110).



FIG. 5. (Color online) (1 - R) as a function of the normal incidence energy for $H_2(v = 0, J = 0)/NiAl(110)$ and $H_2(v = 0, J = 0)/Cu(111)$ at normal incidence and fast grazing incidence along the crystallographic direction [001] and [101], respectively, for $E_i = 400$ eV and several initial molecular vibrational states (A) and (C) and several initial molecular rotational states (B) and (D). Quasiclassical calculations.

We discuss first results for $H_2/Pd(111)$. In Fig. 7(a) we show results for 1 - R as a function of normal incidence energy for $H_2(v = 0, J = 0)$ colliding along the crystallographic direction $[10\bar{1}]$. From this figure we can see that, independent of the total energy, calculations under grazing incidence reproduce the nonmonotonic behavior found at normal incidence. As in the case of slow normal incidence, the nonmonotonic behavior found at fast grazing incidence is due to dynamic trapping. To illustrate this statement, in Fig. 8 we have plotted the percentage of dissociated (1-R) [Fig. 8(a)] and reflected (R) [Fig. 8(b)] molecules after having experienced dynamic trapping (defined by a number of rebounds $n \ge 5$). In Fig. 8(a) we can see that, under fast grazing incidence, dissociated



FIG. 6. (Color online) 1 - R as a function of the normal incidence energy for $D_2(v = 0, J = 0)/\text{NiAl}(110)$ (A) and $H_2(v = 0, J = 0)/\text{Cu}(111)$ (B) at normal incidence and at fast grazing incidence along the crystallographic direction [001] and [101], respectively. $E_i = 400$ eV. Quasiclassical calculations



FIG. 7. (Color online) 1 - R as a function of the normal incidence energy for (A) $H_2(v = 0, J = 0)/Pd(111)$ at normal incidence and at grazing incidence along the crystallographic direction [101] for several total collision energies; (B) $H_2(v = 0, J = 0)/Pd(111)$ at normal incidence and at grazing incidence along several crystallographic directions for $E_i = 400$ eV. Classical calculations.

molecules have been trapped as much as dissociated molecules under slow normal incidence, and in Fig. 8(b) we can see that reflection is a direct process, under both normal and grazing incidence conditions. In conclusion, Fig. 8 shows that dynamic trapping plays the same role for slow normal and for fast-grazing-incidence reactive scattering of H₂ from Pd(111). However, reflectivity (1 - R) as a function of E_n is overestimated (underestimated) at grazing incidence. One possible explanation for this difference is that a trapped molecule can more easily change its incidence direction and thus hit the potential wall (repulsive part of the potential). As a consequence the molecule will be more easily scattered, thus leading to an increase of the total reflectivity. Nonetheless, a



FIG. 8. (Color online) Percentage of molecules trapped ($n \ge 5$) before dissociation. (A) 1 - R and reflection (B) R (reflectivity) for $H_2(v = 0, J = 0)/Pd(111)$ at grazing incidence along the crystallographic direction [$10\overline{1}$], for $E_i = 400$ eV. Classical calculations.



FIG. 9. (Color online) 1 - R as a function of the normal incidence energy for H₂(v = 0, J)/Pd(111), at normal incidence (solid symbols) and at grazing incidence (empty symbols) along the crystallographic direction [101] for several initial rotational states (*J*) and $E_i =$ 400 eV. Classical calculations.

comparison between Figs. 5(a) and 7(a) shows that the level of disagreement is similar to that obtained for $H_2/Cu(111)$ along the $[10\overline{1}]$ direction, whose associated channel has a similar width.

Figure 7(b) shows that the agreement worsens for incidence along directions with narrower channels. In fact, the nonmonotonic behavior of the 1 - R almost disappears when the molecule moves along the narrowest channels. This result suggests that dynamic trapping plays a more important role for narrow channels, because the narrower the channel the more likely a trapped molecule will hit the potential wall and be scattered.

To further analyze the role played by dynamic trapping, we have computed 1 - R curves for rotationally excited molecules, because molecular rotation hinders trapping [45]. Therefore, one can expect that, for highly rotational excited molecules, dynamic trapping is negligible. We show results for rotationally excited molecules in Fig. 9, where we can see that the resemblance between normal and fast grazing incidence improves only slightly when J increases. This result shows that, although trapping plays some role, this is not the main reason for the disagreement between normal and fast-grazing-incidence results. It is the width of the channel along the crystallographic direction the main factor responsible for the quantitative disagreement.

If we perform quasiclassical, instead of classical, calculations (see Fig. 10), we observe that 1 - R as a function of the normal incidence energy behaves monotonically. This behavior is due to the so-called ZPE violation problem that hinders dynamic trapping (see Ref. [46] for details). Apart from this, the resemblance between slow normal and fast grazing incidence results is slightly better than in classical calculations. Also, the agreement is better for wide channels and worse for narrow channels as shown in Fig. 10(a). We can also see in Fig. 10(b) that the agreement does not depend on the initial vibrational state.

We have also studied scattering of H₂ from Pd(110) under fast grazing incidence conditions. As can be observed in Fig. 11 in this case the 1 - R curve as a function of the normal energy at grazing incidence does not reproduce the 1 - R curve at normal incidence. In fact, from Fig. 11 we can see that 1 - R



FIG. 10. (Color online) 1 - R as a function of the normal incidence energy ($E_i = 400 \text{ eV}$). (A) $H_2(v = 0, J = 0)/\text{Pd}(111)$, at normal incidence and at grazing incidence along several crystallographic directions; (B) $H_2(v = 1, J = 0)/\text{Pd}(111)$, at normal incidence and at grazing incidence along the crystallographic direction [101]. Quasiclassical calculations.

behaves monotonically, increasing with normal energy, under grazing incidence conditions. We can also see that, in contrast with results obtained for the other systems studied here, 1 - R results depend strongly on the total collision energy.

This failure for H₂/Pd(110) cannot be attributed to the width of the channel because, in fact, the widest channel in Pd(110) is $\sqrt{2}$ times wider than the widest channel in Pd(111). To understand the differences between H₂(v = 0, J = 0)/Pd(110) and H₂(v = 0, J = 0)/Pd(111) at grazing incidence we should first remind the differences between these two systems at low energy and normal incidence. H₂ molecules trapped on the Pd(111) surface mostly dissociative [46], i.e., dynamic trapping mainly leads to dissociative



FIG. 11. (Color online) 1 - R as a function of the normal incidence energy for $H_2(v = 0, J = 0)/Pd(110)$, at normal incidence and at grazing incidence along the crystallographic direction [$\bar{1}10$], for several total energies. Classical calculations.



FIG. 12. (Color online) Percentage of molecules trapped ($n \ge 5$) before dissociation (A) 1 - R and reflection (B) R (reflectivity) for $H_2(v = 0, J = 0)/Pd(110)$ at grazing incidence along the crystallographic direction [$\bar{1}10$] and $E_i = 400$ eV. Classical calculations.

adsorption, whereas H_2 molecules trapped on the Pd(110) surface can either dissociate or be reflected with almost the same probability [48]. In $H_2/Pd(110)$ at normal incidence, it was found that scattered molecules approach the surface more than in $H_2/Pd(111)$ [50], i.e., a molecule feels more the corrugation when it interacts with Pd(110) than when it interacts with Pd(111). This phenomenon is responsible for the fact that, in $H_2/Pd(110)$, after only 2 rebounds on the surface, the molecule looses memory of its initial incidence conditions, while more than five rebounds are needed to see the same effect in Pd(111). This result indicates that dissociative adsorption as well as scattering of H₂ from Pd(110) after only two rebounds scales with total energy, while a similar scaling requires five rebounds in Pd(111). Taking into account these results for normal incidence, we can guess that, at fast grazing incidence, molecules trapped on Pd(110) will change its incidence direction and will be mostly scattered from the surface before five rebounds, increasing significantly the reflection probability. In order to confirm this hypothesis and to get some insight into $H_2/Pd(110)$ results, we have analyzed dynamic trapping under fast grazing incidence conditions. In Fig. 12 we show the percentage of molecules trapped (defining trapping by a number of rebounds $n \ge 5$) before reflection or dissociation for several selected normal incidence energies (and $E_i = 400$ eV). This figure shows that, under grazing incidence conditions, the number of trapped molecules on Pd(110) is much smaller than on Pd(111), whereas the opposite is observed at normal incidence. Results shown in Fig. 12 seems to indicate that dynamic trapping disappears in Pd(110) because, after a few rebounds (less than five), trapped molecules are easily scattered from it.

IV. CONCLUSIONS

We have studied molecular effects in scattering of H_2 and D_2 molecules under fast grazing incidence conditions colliding with metal surfaces, by means of classical dynamics calculations based on accurate six-dimensional potential energy surfaces, which were obtained by applying a state-of-the-art interpolation method to a set of density functional theory (DFT) data.

Results presented throughout the manuscript show that molecular scattering of H_2 and D_2 colliding with metal surfaces

under fast grazing incidence conditions could be used to evaluate dissociative adsorption saturation values for activated $[H_2(D_2)/NiAl(111)$ and $H_2(D_2)/Cu(111)]$ systems. For these systems dissociative adsorption at slow normal incidence is a direct process, i.e., complex dynamical processes such as dynamic trapping do not play a fundamental role.

For $H_2/Pd(111)$ and also for $H_2/Pd(110)$ the situation is slightly more complex because dynamic trapping should be taken into account. For $H_2/Pd(111)$, dynamic trapping is only important for molecules in their rovibrational ground state. And it only plays a fundamental role for incidence along crystallographic directions with narrow surface atomic channels. In the case of Pd(110), dynamic trapping plays a crucial role, because trapped molecules loose memory of their initial conditions after only two rebounds, which makes $H_2/Pd(110)$ to scale with total energy. Then, a trapped molecule can easily change its incidence direction preventing it from seeing the periodicity of the surface along this direction. As a consequence, momentum (energy) transfer from the parallel longitudinal motion to the parallel transverse motion is now possible and, therefore, momentum transfer from the normal motion to the parallel transverse motion, which is the origin of the observed diffraction, is not the crucial parameter any more. This behavior of the trapped molecules on Pd(110) favors reflection. Furthermore, the higher the parallel logitudinal momentum (energy) the higher the momentum transfer to the parallel transverse motion, which explains why the reflection probabilities are higher for higher total incidence energies.

Finally, the results shown throughout this article suggest that fast grazing incidence experiments might be an appropriate complement to traditional molecular beam sticking measurements, which are limited, from a technical point of view, to low collision energies (see Ref. [55] and references therein). This limitation of traditional sticking experimental setups represents a real handicap to study activated systems, because saturation values for such systems are reached at incidence energies far above the experimental limit. As a consequence, an extrapolation from low-energy-dissociation data is needed, which can lead to an underestimation of the saturation values [39,57]. Therefore, fast-grazing-incidence experiments present a unique opportunity to measure dissociative adsorption saturation values in activated and non activated systems in which dynamics trapping does not play a prominent role.

Systems where these method should work almost perfectly are those with wide channels, such as alloys in which one the atoms barely contributes to surface corrugation, e.g., NiAl(110), or superstructures adsorbed on metal surfaces, e.g., $c(1\times3)$ S/Fe(110), $c(2\times2)$ O/Fe(110) or $c(2\times1)$ O/Ni(110), for which some experimental work with grazing He beams has already been reported [23].

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