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Molecular effects in grazing incidence collisions of H$_2$ with metal surfaces

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Abstract. We have studied the reactive scattering of H$_2$ under grazing incidence conditions and fast collision energies (0.2-2.0 keV), by means of classical dynamics calculations performed with first-principle six-dimensional potential energy surfaces for H$_2$/NiAl(110) and H$_2$/Pd(111). We show that fast light molecules can be used to determine dissociative adsorption probabilities at thermal energies and beyond, from the dissociation threshold up to the saturation limit. The later suggests that this approach is an ideal complement to traditional sticking experiments at thermal energies to determine dissociative adsorption curves up to the saturation limit.

1. Introduction
The interaction of fast atoms and molecules with surfaces has been extensively investigated during the last decades [1–4], both experimentally and theoretically. From the theoretical point of view, classical dynamics methods and model potential energy surfaces have been employed. The main goal of these studies has been to develop analyzing tools in diverse fields such as heterogeneous catalysis, environmental chemistry or material modification. Detailed experimental and theoretical studies of the scattering of fast ions and atoms on surfaces can be found in Refs. [5–9]. In the case of molecular projectiles, it has been found that the energy distribution of scattered atoms resulting from grazing scattering of H$_2^+$ from metal surfaces provides information about the molecule during the scattering process after electron capture [10]. Grazing incidence collisions of neutral molecular projectiles with metal surfaces have been widely studied, both experimentally (where molecular ions neutralize at the surface) and theoretically, by Kleyn and coworkers [11–13], showing an important energy transfer from translational motion to the rotational degree of freedom, as well as the importance of the initial orientational effects on the dissociation of H$_2$ scattered from Ag(111). However, to our knowledge dissociative adsorption of fast neutral molecules colliding with metal surfaces has never been studied neither experimentally nor theoretically.

Recent experimental observations of diffraction of atoms from clean alkali-halide surfaces at grazing incidence (1-3 degrees) and high collision energies (200eV-25keV) [14–16] have opened new possibilities to develop new tools to study structural and dynamical properties of surfaces, decoherence phenomena in quantum scattering or atomic optics in the keV range. Although diffraction of atoms and molecules were already observed in the 1930s [17], it was believed that it could not be observed in the high energy regime, because: (i) the de Broglie wavelength associated with a high incidence energy is much smaller than the typical surface lattice constant and, therefore, much smaller than the typical thermal displacement of the surface atoms,
which introduces decoherence hiding diffraction [18], and (ii) a fast atom has enough energy to produce surface electronic excitations, hence leading to energy dissipation and decoherence [19]. Electronic excitations have been proved to be negligible in wide band-gap insulators [4], but this is not necessarily so in metals. However, very recently, atomic diffraction has been observed in experiments performed on metal surfaces [20–22], proving that the role of electronic excitations is not as important as it could have been anticipated.

The mechanism that explains the physical phenomenon behind these experimental observations was recently proposed by Martín and coworkers [23], to explain why out-of-plane diffraction dominates the diffraction pattern of H$_2$ scattered from Pd(111) for low incidence angles $\theta$ (as defined in Fig. 1), at thermal energies. When the molecule moves along a periodic direction (being $d$ the distance over which the potential replicates), the momentum change along this direction is zero $\left(\Delta k_y = -\frac{\hbar}{m_y} \int_0^d dy \frac{\partial V(y)}{\partial y} = \frac{1}{\hbar} \left[ -V(d,x) + V(0,x) \right] \right)$, therefore any change in the momentum of the projectile is due to the momentum transfer from the slow motion, perpendicular to the surface, to the motion parallel to the surface and perpendicular to the incidence direction $\left(\Delta k_x = -\frac{\hbar}{m_x} \int_0^d dy \frac{\partial V(y)}{\partial x} \neq 0 \right)$. When the wavelength associated to the perpendicular motion is comparable to the surface lattice constant, out-of-plane diffraction is obtained, according to Bragg’s law, if the transverse momentum transfer coincides with a reciprocal lattice vector.

Beyond atomic and molecular diffraction experiments, we propose the use of fast grazing H$_2$ projectiles to study an intrinsic molecular effect: the dissociative adsorption [24]. At thermal energies dissociative adsorption has been extensively studied, both theoretically and experimentally, and it is, at present, rather well understood (see e.g. [25–28] and references therein). However, due to some technological limitations associated with experimental setups at thermal energies, experiments are restricted to very low incidence energies, typically lower than 1.0 eV for H$_2$ and D$_2$ projectiles [29, 30]. This is below the energy values for saturation, and therefore the saturation dissociation probabilities have to be extrapolated from the available data for lower energies, usually leading to wrong results. Experiments at fast grazing incidence open an unique possibility to measure saturation values at thermal energies, considering that, in this kind of experiments, the interaction between the molecule and the surface is governed almost exclusively by the normal energy [14–16], which is of the order of few eVs. In fact, we show here that a plot 1-R as a function of the normal incidence energy, being R the total reflectivity, i.e., the probability of a molecule to be scattered by the surface (at thermal energies 1-R is equal to the dissociative adsorption), reproduces fairly accurately the dissociative adsorption curves at thermal energies.

2. Theoretical approach

To perform this study we make use of classical (C) dynamics, in which the zero point energy (ZPE) of the molecule is ignored, and quasi-classical (QC) dynamics, in which the ZPE of the molecule is included in the calculations. C and QC trajectory methods have given rather good results in the past, in comparison with quantum dynamics and/or experiments, when used to obtain dissociative adsorption [31, 32], rotational excitation [33, 34] and even diffraction [35, 36] probabilities of diatomic molecules interacting with metallic surfaces at thermal energies. In general, the C trajectory method performs better than the QC trajectory one when dealing with non-activated systems (systems for which reaction paths without reaction barriers are found), such as H$_2$/Pd(111), whereas activated systems (systems for which a minimum reaction barrier is always found), such as H$_2$/NiAl(110), are better described by QC dynamics. Within the C and QC dynamics framework, a classical trajectory is computed by solving the Hamilton equations of motion, and the probabilities are obtained as an average over the molecular initial conditions. To simulate the molecular initial conditions a Monte Carlo sampling method is used for each set
of initial parameters \((E_i, v_i, J_i)\), being \(E_i\) the incidence energy, \(v_i\) the initial vibrational state and \(J_i\) the rotational initial state of the molecule. In order to minimize the statistic errors inherent to C dynamics, we perform \(\sim 20,000\) trajectories for each set \((E_i, v_i, J_i)\). For each trajectory the molecule is considered to be reflected whenever \(Z\), distance molecule-surface (see Fig. 1), becomes equal to \(Z_i\), initial distance molecule-surface.

In applying C and QC dynamics we have used the Born-Oppenheimer approximation, i.e., we decouple the motion of the electrons from that of the nuclei. The 6-dimensional (see Fig. 1) potential energy surfaces (PESs), i.e., the molecule-surface electronic interaction for each position and orientation of the molecule over the surface used in this study, were determined previously by applications of the Corrugation Reducing Procedure (CRP) [37] to a set of DFT energy data. For a detailed description of the PESs for \(H_2/Pd(111)\) and \(H_2/NiAl(110)\) see Refs. [38] and [39], respectively.

3. Results

3.1. \(H_2/NiAl(110)\)

![Figure 1](image1.png)

**Figure 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.

![Figure 2](image2.png)

**Figure 2.** \(1-R\), where \(R\) is the reflectivity, as a function of the collision normal energy (for \(E_i=400\) eV) for \(H_2(v_i=0,J_i=0)/NiAl(110)\). Black circles: (thermal) normal incidence results from Ref. [40]. Red squares, blue triangles up, green diamonds, violet triangles down and maroon stars: fast grazing incidence along the direction \(\varphi=0^\circ\), \(\varphi=30^\circ\), \(\varphi=54.74^\circ\), \(\varphi=75^\circ\) and \(\varphi=90^\circ\), respectively. The inset shows the different directions over the surface.

We first show results of \(H_2(v_i=0,J_i=0)\) interacting with \(NiAl(110)\) at grazing incidence and fast collision energies [41]. \(H_2(v_i=0,J_i=0)/NiAl(110)\) at thermal energies is an activated system, i.e., it presents a minimum reaction barrier and, as a consequence, its dissociative adsorption curve presents the typical \(S\) shape [30, 40] (see Fig. 2). In Fig. 2 we have plotted the complementary of the total molecular reflectivity \(1-R\), which corresponds to dissociative adsorption at thermal energy, as a function of the normal incidence energy for a total energy equal to 400 eV (varying \(\theta_i\) from 0.1° to 4.0°) and various incidence directions (see inset Fig. 2), as well as the corresponding dissociative adsorption curve for normal incidence at thermal energies [40]. From this figure we can see that \(1-R\) grazing incidence results mimic quite well the dissociative adsorption probability at thermal energies [30, 40], the agreement being better when the molecule moves along a symmetry direction with low Miller indices. In the later case the collision proceeds in channeling regime [42], where the rows formed by the surface atoms
guide the projectile in its motion along the surface. Channeling is poorer in narrow channels than in wide channels, because for narrow channels the probability that a projectile hits the potential walls (i.e., the repulsive zones of the PES) and get scattered increases, decreasing the agreement between grazing incidence at high energies and normal incidence at thermal energies results. This is the reason why the best agreement is obtained for the H$_2$ colliding along the direction with Miller indices [100], because this direction corresponds to the widest channel that can be followed along the NiAl(110) surface.

**Figure 3.** 1-R, where R is the reflectivity, as a function of the collision normal energy. (a) H$_2$(v$_i$=0,J$_i$=0)/NiAl(110), for several total incidence energies, along the incidence direction $\varphi$=0$^\circ$; (b) H$_2$(v$_i$=0,J$_i$=0)/NiAl(110), for several initial vibrational states, along the incidence direction $\varphi$=0$^\circ$ (red squares) and $\varphi$=90$^\circ$ (blue triangles); (c) H$_2$(v$_i$=0,J$_i$=0)/NiAl(110), for several initial rotational states, along the incidence direction $\varphi$=0$^\circ$ (red circles). Thermal normal incidence results (black circles) have been taken from Ref. [40].

The results shown above are proved to be independent of the total incidence energy, as can be seen in Fig. 3 (a), where we have plotted 1-R as a function of the normal energy for several total incidence energies between 0.2 and 2.0 eV. They also seem to be independent of the initial vibrational and rotational states (see Fig. 3 (b) and (c)). For the sake of comparison with experiments these results are very interesting, because they imply that experimental conditions of the molecular beam would not need to be very restricted, in terms of rovibrational state populations and incidence energies, within a reasonable range, to obtain a meaningful comparison between the experiment and the theory.

**Figure 4.** 1-R, where R is the reflectivity, as a function of the collision normal energy (for $E_i$=400 eV) for D$_2$(v$_i$=0,J$_i$=0)/NiAl(110). Black circles, (thermal) normal incidence results from Ref. [40]. Red squares fast grazing incidence along the direction $\varphi$=0$^\circ$. The inset shows the direction over the surface.

We have also analyzed isotope effects, replacing H$_2$ by D$_2$ projectiles. In Fig. 4 we have plotted 1-R as a function of the normal incidence energy for D$_2$(v$_i$=0,J$_i$=0)/NiAl(110). We can see in this figure that the agreement between results from thermal energies and normal incidence, and high energies and grazing incidence is not as good as for H$_2$(v$_i$=0,J$_i$=0)/NiAl(110). In this case, within the same channel, without taking into account other isotope effects, the heavier the molecule, the higher the probability to hit the potential wall and be scattered, and therefore, the poorer the agreement between both regimes.
3.2. \( \text{H}_2/\text{Pd}(111) \)

The results shown above are not exclusive of \( \text{H}_2/\text{NiAl}(110) \) or any other activated systems [43]; similar results have been found for a non-activated system, i.e., a system with reaction paths free of reaction barriers such as \( \text{H}_2/\text{Pd}(111) \). For this system the dissociative adsorption curve at thermal energies presents a typical non-monotonous behavior [38, 44, 45]. In Fig. 5 we have plotted C and QC 1-R results as a function of the normal energy for \( \text{H}_2(\upsilon_i=0, J_i=0)/\text{Pd}(111) \), along the direction with Miller indices [10\( \overline{1} \)], as well as the corresponding results for normal incidence at thermal energies. From this figure we can see that grazing incidence results obtained by means of C dynamics reproduce qualitatively the non-monotonous behaviour found for normal incidence at thermal energies. The agreement in this case is not as good as for \( \text{H}_2/\text{NiAl}(110) \), which is consistent with the fact that the widest channel in Pd(111) is half of the widest channel in NiAl(100). This also means that the agreement cannot be improved to obtain the correct dissociative adsorption curve by just changing the incidence direction. We also observe from Fig. 5 that QC results at grazing incidence suffer from the same limitation as QC results at thermal energy [38]. Since at thermal energies, QC dynamics does not reproduce the experimental non-monotonous behavior observed for 1-Reflectivity as a function of the incidence energy.

![Figure 5](image)

**Figure 5.** 1-R, where R is the reflectivity, as a function of the collision normal energy (for \( E_i=400 \text{ eV} \)) for \( \text{H}_2(\upsilon_i=0, J_i=0)/\text{Pd}(111) \). Black solid circles and black solid squares, (thermal) C and QC normal incidence results from Ref. [38], respectively. Red open circles and red open squares, C and QC fast grazing incidence, respectively, along the direction \( \varphi=0^\circ \) ([10\( \overline{1} \)]). The inset shows the incidence direction over the surface.

In addition, although these results are not shown here, we have checked that the same level of agreement is obtained as for \( \text{H}_2/\text{NiAl}(110) \), for total energies between 0.2 and 2.0 keV and different initial rotational states.

4. Conclusions

We have shown that molecular reflectivity of fast grazing \( \text{H}_2 \) molecules colliding with metal surfaces can be used to obtain the corresponding dissociative adsorption curve at thermal energy. Our results seem to indicate that, in general, a qualitative agreement between fast grazing and thermal normal incidence can be obtained for 1-R, being R the total reflectivity, for both activated (such as \( \text{H}_2/\text{NiAl}(110) \)) and non-activated (such as \( \text{H}_2/\text{Pd}(111) \)) systems.

The agreement is only quantitative for rather open surfaces. Examples of open surfaces are alloys in which one of the atoms barely contributes to surface corrugation, like the one studied here, NiAl(110), or superstructures adsorbed on metal surfaces, such as \( c(1\times3)\text{S}/\text{Fe}(110) \) and \( c(2\times2)\text{O}/\text{Fe}(110) \) [21]. From our study we conclude that fast grazing incidence experiments could be used as a complement to traditional sticking measurements, which are limited, from a technical point of view, to low collision energies (see, for instance, [29]). This limitation of traditional sticking experiments represents an important handicap to study, for example, activated systems with high reaction barriers, because for these systems the saturation value is reached at collision energies higher than the experimental limit, and extrapolation of low energy dissociation data can lead to wrong saturation values [40, 46]. Thus, fast grazing incidence experiments present a unique opportunity to measure dissociative adsorption saturation values.
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