Dissociative adsorption of N_2 on W(110): Theoretical study of the dependence on the incidence angle

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Abstract

The dissociative adsorption of N_2 on W(110) is studied using classical dynamics on a six-dimensional potential energy surface obtained from density functional theory calculations. Two distinct channels are identified in the dissociation process: a direct one and an indirect one. It is shown that the direct channel is inhibited for low energy molecules ($E_i < 400$ meV) and low incidence angles. The indirect channel includes long-lasting dynamic trapping of the molecule at the surface before dissociation. The dependence of the sticking coefficient on the initial incidence angle is analyzed. The theoretical results compare well with values measured using molecular beam techniques.

Key words:
Gas/surface dynamics, Nitrogen molecule, W surface, dissociative adsorption
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1 Introduction

Metal surfaces are effective chemical agents capable of adsorbing and/or dissociating molecules impinging from the gas phase. Although the actual conditions under which basic research on surface reactivity is developed are highly idealized and far from those required in practical applications [1], there is well-founded hope that the acquired knowledge can significantly help in the understanding of phenomena of practical interest, such as corrosion and heterogeneous catalysis.

Rough surfaces are polycrystalline and their chemical properties are averaged over different faces. This is not particularly important if surface reactivity is almost independent of the specific surface face, but it is relevant if this is not the case. This is one of the reasons for which the dissociation of N_2 on tungsten surfaces has received so much attention: early experimental studies already showed that N_2 on W has the largest crystallographic anisotropies in amounts adsorbed, binding energies and sticking coefficients [2,3]. Although density functional calculations (DFT) show that the process is non-activated in both cases [4,5], the value of the initial sticking probability S_0 above room temperature is very large for the (100) face ($S_0 \approx 0.8$) [6], but roughly three orders of magnitude smaller ($S_0 \approx 3 \times 10^{-3}$) for the (110) face [7].

It has been recently shown that the disparity in N_2 reactivity between both faces arises from the characteristics of the potential energy surface (PES) far from the surface (>3 Å) [5]. The key difference is not the characteristics of the PES well in which the trapping is made, but in the dynamic access to it. For a given impact energy and normal incidence conditions ($\Theta_i = 0°$), the number of available paths in the (100) face is much larger than that in the (110) face. For this reason, thermal energy N_2 molecules dissociate on the (100) face in larger amount than in the (110) face.

In the particular case of the dissociation of N_2 on W(110), there has been much discussion on the effective mechanism driving it [7–14]. The measured dependence of the high temperature sticking on the kinetic energy of the N_2 molecule seems to indicate that this is a direct process, i.e., the N_2 molecules dissociate upon impact [9]. However, the weak dependence of S_0 on Θ_i at high kinetic energy has been also discussed as due to the sampling of an intermediate state prior to dissociation [7]. In previous theoretical analysis [5,15], we concluded that both ways of reasoning are correct: a direct process and an indirect process coexist and compete. The two channels can be defined from the number of rebounds suffered by the incident molecule prior to dissociation in a classical trajectory description of the process.

Further experimental information on the mechanisms driving the dissociation

process can be extracted from the dependence of the sticking on the incident angle of the beam. In the particular case of the W(110) surface, a relatively small dependence of S_0 on the initial polar angle of incidence Θ_i is found: the data show a non-monotonic dependence, which does obey neither normal nor total energy scaling [7]. For impact energies $E_i < 300$ meV, S_0 slightly decreases with Θ_i. For higher energies, S_0 increases with Θ_i up to angles between 30° and 45° and then drops abruptly.

Our purpose in this theoretical work is to analyze the dependence of the N_2 dissociation on W(110) on the incidence angle of the beam. For this purpose, we make use of the six-dimensional (6D) PES interpolated from DFT calculated values that was previously described in Refs. [5,15]. We show the experimental conditions under which each one of the two different dissociation channels mentioned above prevail. We show that the access to the trapping well is very much dependent on this angle, and that it is only the direct channel the one that contributes to the dissociation at high incidence angles. The phase space to approach the surface at low energies is so small that it is only available for molecules impinging with trajectories roughly perpendicular to the surface.

2   Theoretical method

The theoretical method has been explained in detail elsewhere [15], and is only briefly summarized here.

The frozen six-dimensional (6D) adiabatic PES for the N_2/W(110) system is obtained using DFT and the general gradient approximation with Perdew-Wang energy functional (PW91), as implemented in the VASP code [16]. The energy cutoff in the plane-wave basis set is 348.1 eV. Ultra-soft pseudopotentials are used to describe the valence electrons interaction with the ion cores [17]. The adsorbate/substrate system is modelled by a periodic supercell. A 5-layer slab represents the surface. In order to get the equilibrium geometry of the surface in absence of adsorbates, the interlayer distances are relaxed keeping the third layer fix. Then, the energies of the total system formed by the W(110) surface and the N_2 molecule are calculated keeping the surface geometry frozen. Calculations are performed for a (2×2) structure (i.e., 0.25 molecular coverage) and using a $4 \times 4 \times 1$ Monkhorst-Pack grid of $k-$points. We consider 30 configurations of the N_2 molecule at the surface. Each configuration is defined by the molecular axis orientation and the surface site over which the molecular center is placed. The total amount of DFT values calculated in the 6D PES is 5610. Afterwards, the full 6D PES is interpolated using the corrugation reducing procedure [18].

The dynamic interaction between N_2 and the W(110) surface is studied using

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classical trajectory calculations in the adiabatic 6D PES. We have checked that quasi-classical calculations, in which the zero-point energy of the molecule is included, lead to very similar results. Molecules are considered dissociated whenever their internuclear distance reaches a value twice larger than that of equilibrium in the gas phase ($r_{\mathrm{eq}} = 1.11$ Å in our DFT calculation), and they are moving with a positive radial velocity. Results shown in this work are typically obtained using 5000 trajectories per incidence angle and energy.

3 Results and Discussion

General features of the 6D PES for the $N_2/W(110)$ system can be found in Refs. [5,15] and are only briefly summarized in the following. A chemisorption well of roughly 705 meV is found, with the molecule perpendicular over top position at $Z \approx 2.6$ Å and $r \approx r_{eq}$. This potential well can be linked to the γ-N_2 molecular state observed experimentally [19,20], although our theoretical adsorption energy is larger than the measured values. The well is responsible for the dynamic trapping of the molecule at low impact energies. From the bottom of the well, the minimum energy that is necessary to provide to the molecule to make it dissociate is ≈ 350 meV. A simple analysis of the PES based just on two-dimensional elbow plots would lead to the erroneous conclusion that the dissociation of N_2 on $W(110)$ is activated: N_2 molecules impinging over bridge and hollow sites with their molecular axis parallel to the surface require some energy to dissociate. However, classical dynamics calculations of the dynamic process in the 6D PES show that there are non-activated paths going through the well that eventually lead to dissociation.

In order to elucidate the role of any intermediate state in the dissociation process, we study the dynamics of the process using the classical trajectories method and we calculate the sticking S_0 as a function of the incident angle Θ_i. Furthermore, we analyze the obtained theoretical results in the following way. We calculate the number of rebounds n_r suffered by the N_2 molecule along the trajectory in its path to dissociation. A rebound is defined as a change from negative to positive sign in the perpendicular component of the N_2 velocity. We split the dissociation probability into a 'direct' component and an 'indirect' component. The former corresponds to trajectories for which $n_r < 4$ and the latter corresponds to trajectories for which $n_r \geq 4$. The actual value of n_r selected to split the two mechanisms is arbitrary, but our conclusions do not depend on this choice, provided that reasonable values are taken.

The 'direct' and 'indirect' contributions to the sticking coefficient S_0 are plotted in Fig. 1 as a function of the incident energy E_i and for different values of Θ_i. The results are compared with experimental data measured at a surface temperature of 800 K [7,11]. At normal incidence, the 'direct' contribution is

dominant for $E_i > 750$ meV, and almost vanishes below $E_i < 400$ meV. In the latter low energy range, the 'indirect' process rules. It is related to trajectories that spend a large amount of time dynamically trapped about the chemisorption well and eventually dissociate. This indirect channel could be interpreted as a precursor state before dissociation. We remark the dynamical aspect of this state, in contrast to the usual picture of a static precursor state. We have checked that the typical time spent by the molecule in each rebound τ_r is approximately $\tau_r \approx 0.16$ ps, and that τ_r is independent of E_i. Trajectories leading to dissociation for $E_i < 400$ meV correspond to molecules that spend several picoseconds (between 1 and 8 ps for $0.025 < E_i < 400$ meV) bouncing in the vicinity of the chemisorption well before becoming dissociated.

For higher incidence angles, the indirect channel gradually fades, and at the highest angle considered, $\Theta_i = 60°$, the situation is drastically changed. Dynamical trapping is almost completely inhibited for these angles and the 'direct' process is the main responsible for the sticking. For low E_i, the access to the chemisorption well is only accessible to those molecules that approach the surface following normal trajectories ($\Theta_i \approx 0°$), and with the molecular axis oriented perpendicularly to the surface ($\theta \approx 0°$). Hence, off-normal incidence trajectories get reflected relatively far from the surface ($Z \approx 3$ Å).

Although the behaviour is qualitatively correct, comparison of our theoretical results with the experimental measurements of Refs. [7,11] show some discrepancy whenever the indirect channel contributes. We partially attribute this difference between the theoretical and experimental results to a possible overestimation of the indirect channel contribution to the theoretical sticking. The overestimate is most likely due to inaccuracies in the description of the PES in the narrow region in which the exit of the well toward dissociation takes place. At normal incidence, the theoretical values of S_0 turn out to be extremely sensitive to the details of the PES in that region [15]. For this reason, we focus into the range of energies $E_i > 400$ meV for our subsequent analysis on the angular dependence of S_0.

The dependence of the sticking S_0 on the incidence angle Θ_i is shown in Fig. 2 for several values of E_i. The behaviour is similar for all of them: a slight increase of S_0 as the incident angle goes off-normal, and a sudden decrease for higher values of Θ_i. Neither total nor normal energy scaling is found. In other systems, such as $H_2/Pd(111)$, this behaviour off standard scalings was found to be a consequence of the competition between the direct and the indirect channels [21]. Nevertheless, we have performed additional calculations (not shown here) that prove that the general trends for the dependence of the theoretical sticking values on Θ_i are similar if the indirect contribution to S_0 is neglected and only the direct channel is computed. Hence, in the present case, the peculiar angular dependence is not the result of two different dissociation channels adding up.

The theoretical results on the dependence of S_0 on Θ_i qualitatively reproduce the measured experimental data. Nevertheless, the comparison should be made with some caution. We have checked that the theoretical S_0 values have a certain dependence on the azimuthal angle of incidence Φ_i, in particular for $\Theta_i = 45°$ and $\Theta_i = 60°$. However, since we do not know the exact Φ_i under which the experimental measurements were performed, our results for S_0 are obtained by making an angular average over Φ_i. Under these conditions, we consider the qualitative agreement between theory and experiments as satisfactory enough.

4 Summary and Conclusions

The dissociation of N_2 on W(110) is a non-activated process that can proceed through two distinct channels, noted as direct and indirect. The indirect channel requires dynamic trapping of the N_2 molecule over the top site before dissociation. The direct channel is linked to trajectories reaching close distances to the surfaces without much transfer of momentum in the direction parallel to the surface. At low impact energies ($E_i < 400$ meV) and $\Theta_i = 0°$, the N_2 dissociation is ruled by dynamic trapping. But for higher incident angles and/or higher energies, the trapping can be inhibited and the dissociation restricted to the direct channel.

The dependence of S_0 on the initial angle of incidence Θ_i shows a non-monotonic distribution that follows neither normal nor total energy scaling. The non-monotonic dependence is attributed just to the direct channel and not to a competition between different channels. Our calculations using classical dynamics in a 6D PES are able to qualitatively reproduce the general trends of the angular dependence. 'Hot' angles for which dissociation is favoured are clearly visible both in the experimental and in the theoretical results. Nevertheless, further investigation on the role of the initial azimuthal angle Φ_i is needed for a deeper understanding of the process.

5 Acknowledgements

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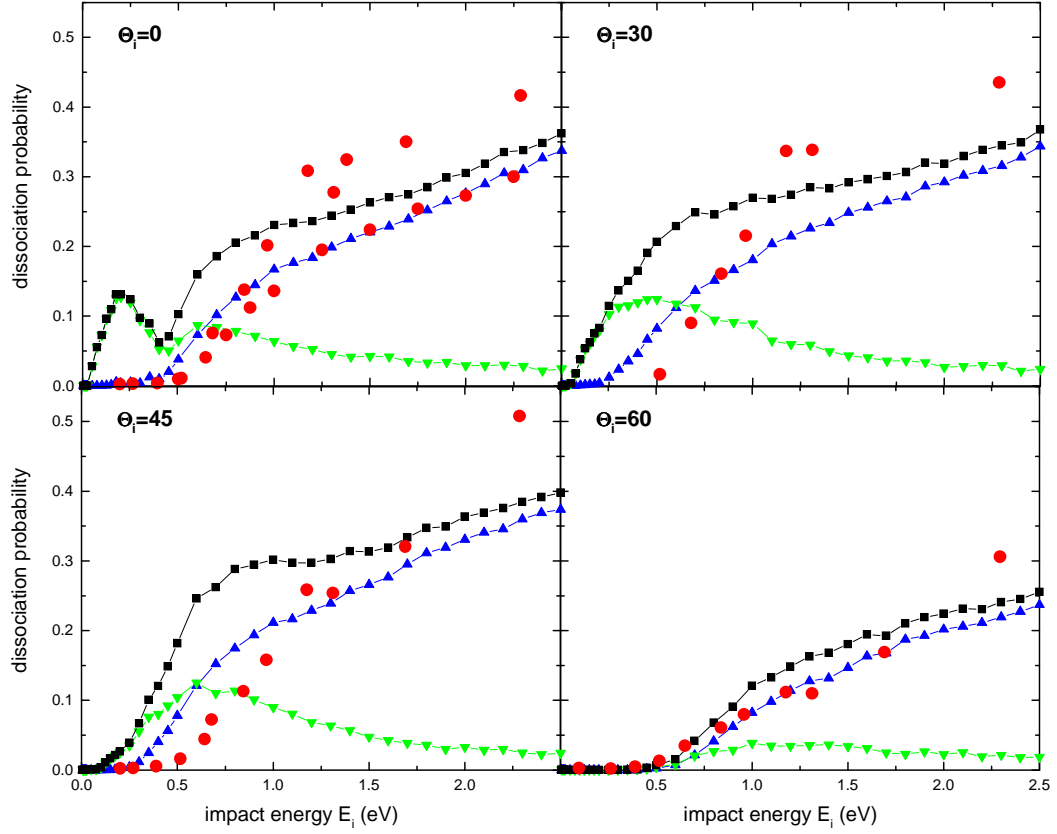[21] C. Díaz, H. F. Busnengo, F. Martín, and A. Salin, J. Chem. Phys. **118** (2003) 2886.

Fig. 1. Dissociative sticking probability S_0 as a function of the initial kinetic energy of the N_2 molecule E_i in eV, and for various incidence angles. Black squares are theoretical results. Red circles are the experimental results of Refs. [7] and [11]. Blue up-triangles show the direct contribution to S_0 and green down-triangles show the indirect contribution. Lines are shown to guide the eye.
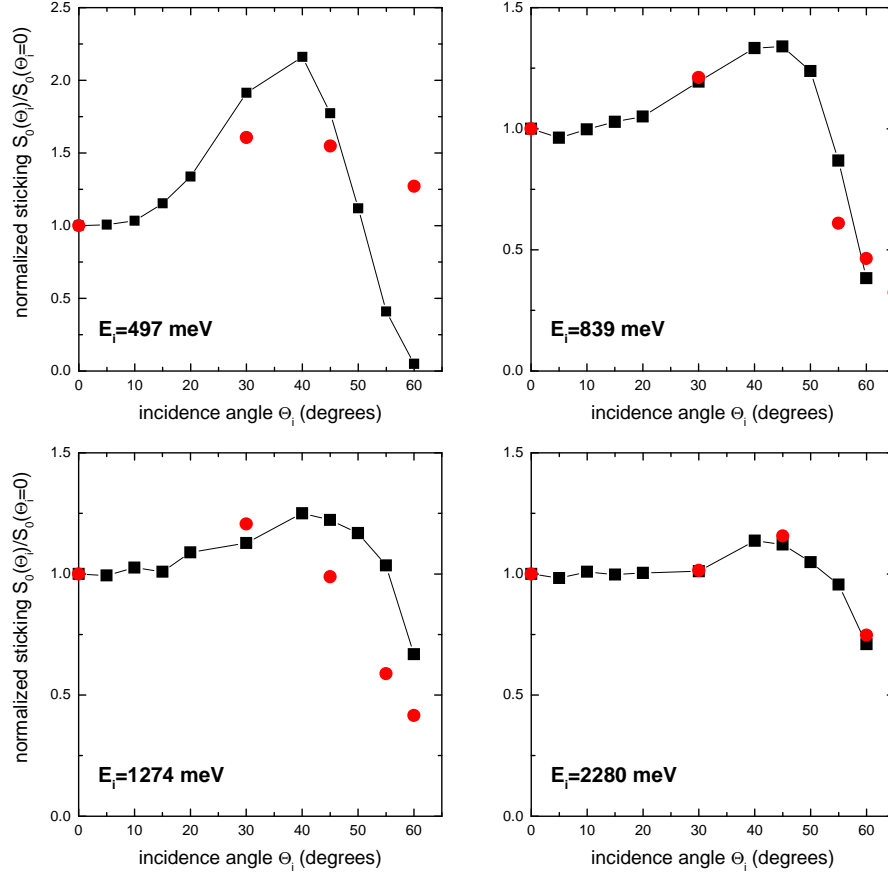
Fig. 2. Dissociative sticking probability $S_0(\Theta_i)$ for N_2 on W(110) as a function of the initial angle of incidence of the beam Θ_i (in degrees) and for various impact energies E_i. $S_0(\Theta_i)$ is normalized to the value at normal incidence $S_0(0)$. Black squares are the theoretical results (with a line drawn to guide the eye). Red circles are the experimental data of Ref. [7]. Notice the difference in scale for the ordinates for $E_i = 497$ meV.