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Dissociative adsorption of N_2 on W(1 1 0): Theoretical study of the dependence on the incidence angle

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Abstract

The dissociative adsorption of N_2 on W(1 1 0) 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.

Keywords: 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 (1 0 0) face ($S_0 \approx 0.8$) [6], but roughly three-orders of magnitude smaller ($S_0 \approx 3 \times 10^{-3}$) for the (1 1 0) 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 (1 0 0) face is much larger than that in the (1 1 0) face. For this reason, thermal energy N_2 molecules dissociate on the (1 0 0) face in larger amount than in the (1 1 0) face.

In the particular case of the dissociation of N_2 on W(1 1 0), there has been much discussion on the effective

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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(1 1 0) 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(1 1 0) 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(1 1 0) 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(1 1 0) 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(1 1 0) surface is studied using 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 ($r_{eq} = 1.11$ 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(1 1 0) 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(1 1 0) 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 $n_r \geqslant 4$. The actual value of n_r selected to split the two mechanisms is arbitrary,