Why N_2 Molecules with Thermal Energy Abundantly Dissociate on W(100) and Not on W(110)

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Low-energy N_2 molecules easily dissociate on W(100) but not on W(110). In this Letter, the six-dimensional potential energy surface for the dissociation of N_2 molecules on W(110) has been determined by density functional calculations. Results are compared to those of N_2 dissociation on W(100). The difference in reactivity between the two faces is shown to arise from the characteristics of the potential energy surface far from the surface (> 3 Å) and not from the properties of a precursor well or those of the final atomic adsorption sites.

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Over the last years, the combination of experimental molecular-beam techniques [1–3] and refined theoretical studies based on *ab initio* calculations [4–7] have led research on the chemistry of metal surfaces to a new stage, in which detailed investigations of the kinetics and dynamics of molecular reactivity at surfaces are possible. Chemical reactivity on a surface depends on numerous factors, including temperature and pressure conditions [8]. There is also an intrinsic feature of the metal surface that can play a dramatic role in its chemical activity, namely, the crystal surface structure.

An emblematic example of this is the dissociation of nitrogen molecules on some metal surfaces, such as iron and tungsten. N_2 dissociation is, for example, the rate limiting process in the synthesis of ammonia on iron surfaces. Under low pressures, the dissociation probability changes by orders of magnitude according to crystal face, decreasing in the sequence (111), (100), (110) [9]. It has been noted that the most reactive (111) surface is the one exposing metal atoms with coordination 7 [10]. However there is not even a hint on what could be the relation between this observation and reactivity. Studies of atomic nitrogen adsorption states do not shed any light since similar adsorption properties are found for the (111) and (110) surfaces [11], those associated with maximum and minimum reactivity, respectively. The main drawback in studying theoretically N_2 dissociation on Fe is that the dissociation probability is very small ($<5 \times 10^{-6}$), which makes any evaluation extremely challenging.

A similar sensitivity to surface structure is observed for the dissociation of low-energy N_2 beams on W surfaces. While dissociation is considerable for vanishingly small beam energy on the W(100) surface [12], it is roughly 2 orders of magnitude smaller at $T = 800$ K on the W(110) face [13] (see Fig. 1). This remarkable dependence on surface structure remains unexplained. It has been shown [14] that the high reactivity on the (100) surface is associated with the fact that the $N_2/W(100)$ system is non-activated; i.e., there exist paths leading to dissociation without any barrier. The efficiency of dissociation in this case is due to dynamic trapping: when approaching the surface, energy is transferred from perpendicular motion to other degrees of freedom so that the molecule cannot "climb" back the potential slope toward vacuum. On the (110) surface of W, however, the dissociation probability is of the order of a few 10^{-3} for beam energies below 300 meV; it then increases rather quickly towards 0.2 until 1 eV and goes on rising more smoothly until a value of 0.3 for an energy of 2.5 eV [13]. This behavior is usually considered as typical of that of an activated system; i.e., no path leads to dissociation without overcoming a barrier [13,15–18]. According to this picture, the unequal role of

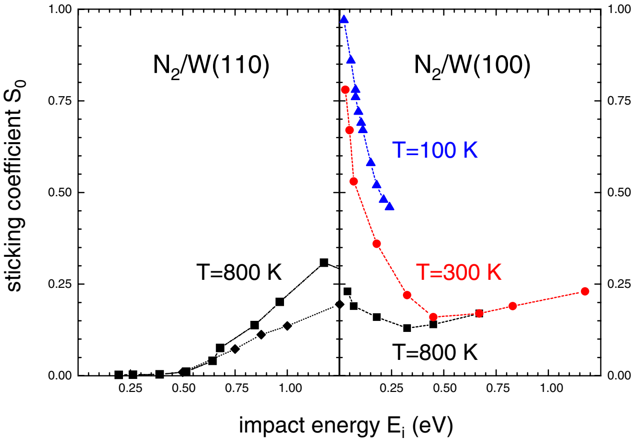

FIG. 1 (color online). Experimental sticking coefficient S_0 for N_2 on W(110) (left panel) and W(100) (right panel) as a function of impact energy for normal incidence. Data are extracted from Refs. [12,25] (100) and [13,18] (110). Surface temperature is 800 K (black squares and diamonds), 300 K (red circles), and 100 K (blue triangles). Lines are drawn to guide the eye.

the (100) and (110) faces of W on the dissociation of low-energy N_2 molecules would be a direct consequence of the nonactivated and activated characters, respectively, of the two processes.

In this Letter we use density functional theory (DFT) calculations and classical dynamics to show that the large difference in reactive behavior between the (100) and (110) faces at low energies is entirely determined by the shape of the potential energy surface (PES) far from the surface (above 3 Å). The explanation therefore lies neither on the geometry and energy of the final state (2 N atoms on the surface) nor on the presence or absence of an intermediate well in which the molecule could be temporarily trapped. Such a well exists for both the (110) and (100) faces. The crucial point is that only for the latter is the well accessible to low-energy molecules. We will also show that there are nonactivated paths to dissociation in the interaction of N_2 with W(110) surfaces. Nevertheless, the value of the sticking coefficient S_0 at low impact energies E_i is very small. This result contradicts the standard along which dissociation probabilities that increase with the incident kinetic energy are the result of a direct activated process. Furthermore, it contradicts the common assumption that intermediate states (such as dynamic trapping in our case) and nonactivated paths always result in large values of the sticking coefficient at very low energies.

A brief description of the theoretical method follows. We calculate the frozen six-dimensional (6D) adiabatic PES for the N_2/W(100) system. For that purpose, we use DFT and the general gradient approximation with Perdew-Wang energy functional PW91, as implemented in the VASP code [19]. Ultrasoft pseudopotentials are used to describe the interaction with the ion cores [20]. A periodic supercell models the adsorbate/substrate system. The surface is represented by a 5-layer slab, and the distance between slabs is 18.2 Å. Calculations are performed for a (2×2) structure (i.e., 0.25 coverage) and using a $4 \times 4 \times 1$ Monkhorst-Pack grid of k points.

The total number of DFT energies calculated in the 6D PES is 5610. They represent 30 configurations of the N_2 molecule at the surface. Each configuration is defined by a molecular axis orientation and the surface site over which the molecular center of charge is located. For each configuration, we calculate an 11-point grid in r space and a 17-point grid in Z space, where r is the internuclear distance and Z is the distance between the molecular center of charge and the W surface. The evaluation of any point on the 6D PES is achieved through interpolation using the corrugation reducing procedure [21].

The dynamic interaction between N_2 and the W(110) surface is studied using classical trajectory calculations in the adiabatic 6D PES. Results allowing or not for zero point motion in the initial conditions are very similar. Molecules are considered dissociated whenever their internuclear distance reaches a value twice larger than that of equilibrium in the gas phase ($r_{\text{eq}} = 1.11$ Å in our DFT calculation), and they are moving with a positive radial velocity.

Theoretical results for the sticking probability $S_0(E_i, \Theta_i)$ are plotted in Fig. 2 as a function of N_2 initial kinetic energy E_i and for two incidence angles, $\Theta_i = 0°$ and $\Theta_i = 60°$ with respect to surface normal. The value of $S_0(E_i, \Theta_i)$ for given E_i and Θ_i is typically obtained with 5000 trajectories. Results are compared with experimental data for a surface temperature of 800 K [13,18]. We have also performed test calculations of S_0 including temperature effects through the generalized Langevin oscillators model, in a way similar to Ref. [22], and the results do not significantly deviate. Notice the general agreement between theory and experiment, even though our calculations are performed for a rigid surface, except for the theoretical bump found between 100 and 500 meV at $\Theta_i = 0°$.

The obtained dissociation probability is an increasing function of E_i and falls to negligible values (of the order of 10^{-3}) for very small E_i. The dependence of the experimental values of S_0 on E_i, qualitatively described by our frozen-surface theoretical calculation, is commonly considered as indicative of an activated direct process. Following the trajectories of the N_2 molecules that dissociate on the W(110) surface at low energies, we have found that there are nonactivated paths leading to dissociation in the 6D PES. We show in Fig. 3 the value of the PES along one of these trajectories, corresponding to an impact energy of 100 meV. The geometry of the system at some snapshots of the trajectory is sketched in Fig. 3 as well.

Some of the most prominent features of the reaction path are apparent in Fig. 3. We have carefully checked that no barrier in the entrance channel is found at large distances from the surface, in opposition to the calculations of Ref. [23]. We find a precursor well of roughly $E_c \approx 705$ meV at $Z \approx 2.6$ Å for molecules with vertical orientation approaching top positions at the surface. Statistics

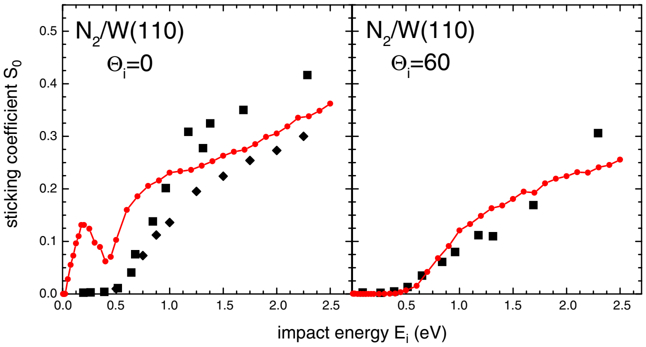

FIG. 2 (color online). Dissociative sticking probability S_0 for N_2 molecules on W(110), as a function of impact energy E_i (in eV). Incidence angles with respect to the surface normal are $\Theta_i = 0°$ (left panel) and $\Theta_i = 60°$ (right panel). Small red circles: our theoretical results (line is shown to guide the eye). Experimental results are from Refs. [13] (squares) and [18] (diamonds).

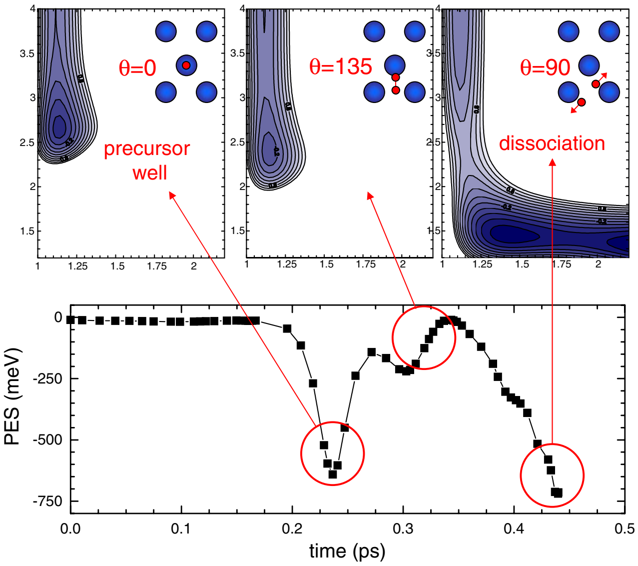

FIG. 3 (color online). Potential (in meV) as a function of time (in picoseconds) along a trajectory leading to dissociation, for N_2 on W(110). The geometry of the system at some points of the trajectory is represented in the upper panels. For each geometry, the PES is also plotted as a function of radial coordinate (horizontal axis) and distance from the surface (vertical axis). The energy difference between contour lines is 0.2 eV. Distances are in Å.

over dissociating trajectories lead us to conclude that the low-energy N_2 molecules that eventually dissociate must approach the surface in a roughly vertical orientation and on top of a W atom: they are temporarily trapped in the precursor well, and then move towards either bridge or hollow sites, at the same time that they rotate. The final step in N_2 dissociation is usually found at distances from the surface of roughly $Z = 1.3$ Å and with the molecular axis parallel to the surface.

Our theoretical analysis shows that a direct process and an indirect process coexist and compete in the dissociation of N_2 on W(110). For beam energies below roughly 500 meV and normal incidence, the indirect process, in which the molecule is dynamically trapped in the precursor well, is the dominant. Trajectories leading to dissociation through this indirect channel correspond to molecules that typically spend several picoseconds (between 1 and 8 ps for $25 < E_i < 400$ meV) bouncing in the vicinity of the well before dissociating. In general, the trapped molecules can leave the well either toward dissociative adsorption or back into the gas phase. We have verified that the balance between these two processes is extremely sensitive to details of the PES in the vicinity of the well. More precisely, small differences in the PES in the narrow region that allows the trapped molecules to channel toward dissociation significantly change the dissociation probability for $100 < E_i < 400$ meV and normal incidence, and our results should be taken with caution under these particular conditions. However, the values of the dissociation probability for $E_i < 100$ meV are rather insensitive to the PES characteristics at the well position. In this low-energy range, the crucial point is the dynamics at distances relatively far from the surface ($Z \approx 3.25$ Å), for which our theoretical results are robust.

For energies above 500 meV, dissociating molecules are not constrained to approach the surface over the top site and do not suffer a significant number of rebounds along their trajectory. Dissociation can thus be considered as direct in this energy range. For off-normal incident angles, the access to the precursor well is restrained over the full energy range considered. The indirect channel is therefore quenched, as can be seen in Fig. 2 for $\Theta_i = 60°$.

The PES characteristics for the $N_2/W(100)$ system exposed so far are not intrinsically different from those of N_2 on W(100). However, the dissociation probability S_0 for thermal N_2 molecules impinging on the W(110) face at $T = 800$ K is 2 orders of magnitude smaller than that of the W(100) face. This spectacular difference in reactivity in the thermal energy range is a consequence of the PES properties at large distances from the surface. The (110) PES is only attractive for the approach of molecules on top of a W atom with axis nearly normal to the surface. This is completely different from the behavior of the (100) PES, in which the number of paths allowing the molecule to approach the surface above 3 Å is much larger [14].

Figure 4 shows that, for kinetic energies below 100 meV, most of the N_2 molecules incident on W(110) are already reflected above $Z = 3.25$ Å. A large percentage (between

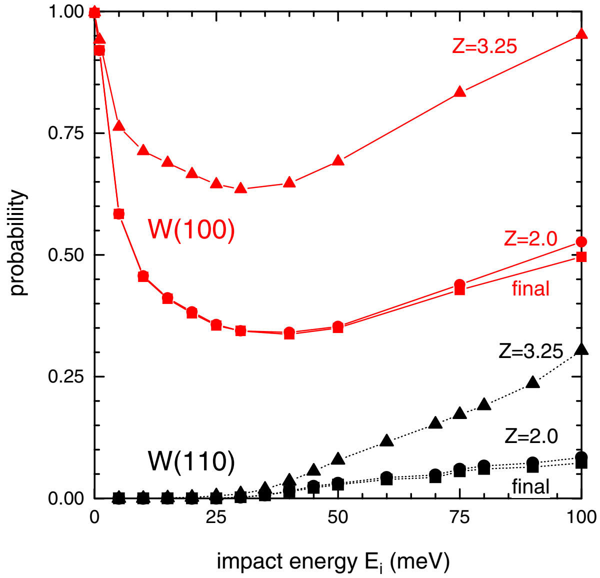

FIG. 4 (color online). Probability for N_2 molecules to reach a given distance Z from the W surface, as a function of normal impact kinetic energy (in meV) for 5000 trajectories. Up-pointing triangles and circles correspond to $Z = 3.25$ Å and $Z = 2$ Å, respectively. Squares show the final value of the sticking coefficient S_0. Lines are drawn to guide the eye: (red) solid lines refer to W(100) and (black) dotted lines to W(110).

25% and 40%, depending on the energy) of the N_2 molecules that are able to approach the surface below this point will be eventually dissociated. A similar conclusion can be extracted from the (100) data: the qualitative dependence of S_0 as a function of E_i is already reproduced by the molecules reaching $Z = 3.25$ Å. However, for this surface structure, the number of N_2 molecules that are able to find energetically favorable paths to approach the surface is significantly larger.

In summary, our DFT calculations show that the dissociative adsorption of N_2 molecules at W(110) surfaces is a nonactivated process. This is in contrast with the common assumption that identifies increasing values of S_0 as a function of E_i with direct activated processes. The dissociative sticking involves two different mechanisms: in one of them, dissociation can be considered as direct, and in the second, the N_2 molecules are dynamically trapped for times of up to tens of picoseconds. Nevertheless and contrary to expectations, the sticking coefficient S_0 at very low energies ($E_i < 100$ meV) is tiny, and 2 orders of magnitude smaller than that of the W(100) face. This striking difference in reactivity between surface structures is not a consequence of the final state in the chemisorption process, a factor that is often stressed for these reactions [24]. The big difference in the value of S_0 is already determined at distances of $Z = 3.25$ Å from the surface and arises from the behavior of the PES in the entrance channel. The access to the precursor well, from which dissociation may eventually take place, is possible in the (110) surface for just a small number of trajectories while it is widely open in the (100) surface. This strong influence of the long-distance interaction on surface reactivity introduces an unconventional and alternative view on the mechanisms driving gas-surface reaction dynamics in the thermal energy range, precisely the regime under which most technological applications are conducted.

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