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Dynamics of adsorption and dissociation of N$_2$ in a monolayer of iron on W(110)

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Abstract

We study the adsorption dynamics of N$_2$ on an expanded monolayer of Fe grown pseudomorphically on W(110). To this aim we perform molecular dynamics simulations in a six-dimensional potential energy surface calculated within density functional theory. Our results show that N$_2$ dissociation on this surface is a highly activated process with an energy barrier of around 1.25 eV. Regarding molecular adsorption, we find that the energetically most favorable adsorption well corresponds to a parallel orientation of the molecule with an adsorption energy of around 520 meV. However, at low molecular energies and surface temperatures, the molecules preferentially adsorb vertical to the surface with an adsorption energy of around 480 meV. A comparative analysis with the results previously obtained in a clean Fe(110) surface shows that while surface strain favors molecular adsorption of N$_2$ in this system, it impedes dissociative adsorption. The former is consistent with the experimental observations showing that the inertness of Fe(110) towards N$_2$ uptake is reduced in the strained surface. The latter leads us to suggest that the experimental observation of dissociated atomic N in the strained surface when increasing surface temperature must be related to the presence of step/defects at the surface.

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I. INTRODUCTION

One challenge in surface science is to control the chemical reactivity of surfaces towards the different chemical species. In this context, surface strain has been extensively investigated during last years [1–12]. Its practical realization can be achieved by the pseudomorphic growth of ultrathin metallic films on the surface of a different metal [1, 5]. The lattice constant of the overlayer is thus stretched to fit that of the underlying substrate and the surface electronic properties can be substantially modified.

Generally, expanded metal surfaces are expected to be more reactive than the unstrained surfaces of the same metal. In the case of transition metals, this has been often rationalized within the so-called $d$-band model [13]. The underlying reasoning is that in an expanded lattice the overlap of atomic orbitals is reduced with the subsequent narrowing and up-shift of the $d$-band towards the Fermi level. The closeness of the center of the $d$-band to the Fermi level implies a more reactive surface, which is characterized by larger chemisorption energies and lower dissociation barriers.

Despite its simplicity, the $d$-band model has explained adsorption properties and allowed to make predictions for a variety of systems [3, 7, 13, 14]. However, there are also examples showing that the relation between strain and reactivity is in some cases too complex to be adequately described by this model [6, 8, 9, 11]. Therefore, to understand the effect of strain in the reactivity of a specific gas/surface system a complete characterization of the multidimensional potential energy surface (PES) is required together with a proper account of the dynamics.

In this work we focus on the dynamics of adsorption and dissociation of $N_2$ molecules on a expanded monolayer of Fe grown on a W(110) surface. Our study is motivated by the experimental results of Homann et. al. [1] that showed that the inertness of Fe(110) towards $N_2$ adsorption and dissociation is strongly reduced on thin layers of Fe grown on W(110). It has been shown that the first layer of iron on W(110) grows pseudomorphically [15, 16], i.e., with the same lattice parameter as the substrate. Due to the large lattice mismatch of about 10% derived from the different lattice constants of W ($a_W = 3.17$ Å) and Fe ($a_{Fe} = 2.87$ Å) [17], the expanded Fe monolayer on W(110) constitutes an optimal system to study the effect of strain in reactivity.

Interest of the $N_2$/Fe system relies on the fact that Fe is the traditional catalyst for am-
monia synthesis for which N₂ dissociation is the rate-limiting step [18, 19]. In a recent work we studied the reaction dynamics of N₂ on the Fe(110) surface [20]. We showed that the low reactivity of the Fe(110) towards dissociation of N₂ is the result of a high activation barrier of about 1.1 eV together with a very narrow reaction path. Additionally, we identified two different molecular adsorption sites: one with the molecule oriented vertical to the surface atop a surface Fe atom and a second adsorption site in which the molecule is parallel to the surface with the center of mass over the hollow site. Although this second adsorption site is energetically more favorable, our dynamics simulations showed that molecules preferentially adsorb over the top-vertical site at low incident energies and surface temperatures. These results were rationalized in terms of the energy barriers that the molecule needs to overcome in order to be adsorbed: 150 meV for adsorption on the top-vertical well versus 250 meV for adsorption on the hollow-parallel well.

Thus, the purpose of this study is to explore how the characteristics of the N₂/Fe(110) system are modified in the case of N₂ interacting with an expanded Fe monolayer grown on W(110). A study on the differences for dissociative and molecular adsorption between both surfaces has been presented in ref. 21. A more thorough analysis of the problem and of the characteristics of the N₂/Fe/W(110) system is provided in the present work. The outline of the paper is as follows. In Section II, we describe in detail all the steps followed to construct from density functional theory (DFT) calculations, the adiabatic six-dimensional (6D) PES for N₂/Fe/W(110). The static properties that characterize the interaction between N₂ and the Fe/W(110) surface, such as the adsorption states and the reaction paths to dissociation are also analyzed there. We end Section II with a qualitative and quantitative comparison between the N₂/Fe/W(110) and the N₂/Fe(110) PESs. In Section III, the dynamics of dissociative and molecular adsorption of N₂ on Fe/W(110) is presented and compared with those obtained for N₂ on Fe(110). The results are discussed in connection with the experimental observations of Homann et al. [1]. In Section IV, the adsorption energies and energy barriers of the N₂/Fe(110) and N₂/Fe/W(110) PESs are analyzed in terms of the d-band model, here adapted to the specificities of the N₂ molecule and the magnetic nature of the substrate. Furthermore, the complex changes induced by the heteroepitaxial strain for N₂ dissociation are rationalized in terms of the topographical differences between the unstrained Fe(110) and the largely expanded (10%) Fe monolayer. Finally, the main conclusions of this work are summarized in Section V.
II. CALCULATION OF THE ADIABATIC POTENTIAL ENERGY SURFACE

The interaction of N\(_2\) with the frozen (static) Fe/W(110) surface is described with an adiabatic 6D PES that depends on the six degrees of freedom of the molecule. The latter are described by the following coordinates: The position of the center of mass of the molecule, \(\mathbf{R}=(X,Y,Z)\), the molecular interatomic distance \(r\), and the molecular orientation relative to the surface determined by the polar \(\theta\) and azimuthal \(\varphi\) angles (see Fig. 1). The continuous representation of the 6D PES is obtained from the interpolation of 20,801 DFT energy values using the *corrugation reducing procedure* (CRP)[22]. The DFT data are calculated with the general gradient approximation and the RPBE exchange correlation functional [23] as implemented in the “Vienna *ab initio* simulation program” (VASP) [24, 25]. The energy cut-off in the plane-wave expansion is 400 eV. The fractional occupancies are determined through the broadening approach of Methfessel and Paxton with \(N=1\) and \(\sigma=0.4\) eV.

Using these parameters and a \(15 \times 15 \times 15\) Monkhorst-Pack \(\mathbf{k}\)-points mesh [26], the calculated lattice constant for bulk W is \(a=3.165\ \text{Å}\). The corresponding bulk interlayer spacing of \(d = 2.238\ \text{Å}\) along the (110) direction is in good agreement with the nominal value of \(d = 2.23\ \text{Å}\) [27]. The Fe/W(110) surface is modeled by a periodic slab constituted by six layers of W and one layer of Fe, a \((2 \times 2)\) surface structure, and a supercell vector along the surface normal (\(z\)-axis) of 21 \(d\), from which 15 \(d\) correspond to vacuum. This supercell size assures that the undesirable interactions among the periodically repeated molecules are negligible, as it was demonstrated in ref. 20. Additionally, it provides an accurate description of the physical properties of the Fe/W(110) interface, as shown below. The Brillouin-zone integration is performed with a \(4 \times 4 \times 1\) Monkhorst-Pack grid of special \(\mathbf{k}\)-points. Next, the surface is relaxed by keeping fixed the central layer. In the relaxed structure the distance between the Fe and topmost W layer is 1.97 Å, which represents a contraction of around 12% respect to the interlayer spacing of W(110). Additionally, the distance between the first and second W layers \(d(W_1-W_2)\) is increased around 1% relative to the reference value. These results compare well with previous calculations that predict a contraction in \(d(\text{Fe-W}_1)\) of 12.1%[28] and 12.9%[29], as well as an expansion in \(d(W_1-W_2)\) of 0.9%[28] and of 0.1%[29]. Experimentally, the distance between the Fe and W topmost layer is contracted in a 13%[30] in quite good agreement with the aforementioned results. Regarding the magnetic properties, the surface magnetic moment per Fe atom of the topmost layer is \(2.53\mu_B\), which
coincides with the experimental value of ref. 31 and is close to the value of 2.56μB provided by previous calculations [32].

The DFT energies used to construct the continuous 6D PES are calculated for 31 different configurations of the N2 molecule. A configuration is defined by the molecular orientation (θ, ϕ) and the position of the molecular center over the surface unit cell (X,Y). For each configuration, a two-dimensional (2D) (r,Z)-cut of the 6D PES is obtained with r varying from 0.71 Å to 2.31 Å in a non-equidistant grid of 11 points, and Z varying from 0.0 to 6.0 Å by steps of 0.1 Å. The energy of all the configurations for a given r value is basically constant for Z ≥ 6 Å. Thus, the zero reference energy in the N2/Fe/W(110) PES is taken for the molecule at the equilibrium bond length r = req = 1.11 Å and located at 6 Å from the surface. The potential energies are calculated for the following configurations (see Fig. 1(b)):

- Six configurations over top site (X=0, Y=0): θ=0°; θ=90° with ϕ=0° and ϕ=54.74°; and θ=45° with ϕ=0°, ϕ=54.74° and ϕ=90°.
- Six configurations over hollow (hw) site (X=a/2, Y=0): θ=0°; θ=90° with ϕ=0°, ϕ=54.74° and ϕ=90°; and θ=45° with ϕ=0° and ϕ=90°.
- Six configurations over bridge (br) site (X=a/4, Y=a√2/4): θ=0°; θ=90° with ϕ=0°, ϕ=54.74°, and ϕ=125.26°; and θ=45° with ϕ=54.74° and ϕ=125.26°.
- Six configurations over short top-hollow (short-th) site (X=a/4, Y=0): θ=0°; θ=90° with ϕ=0° and ϕ=54.74°; and θ=45° with ϕ=0°, ϕ=90°, and ϕ=180°.
- Seven configurations over long top-hollow (long-th) site (X=0, Y=a√2/4): θ=0°; θ=90° with ϕ=90° and ϕ=35.26°; and θ=45° with ϕ=0°, ϕ=54.74°, ϕ=90°, and ϕ=270°.

Figure 2(a) shows the variation of the potential energy with Z for various configurations of the N2 molecule with req. Note the presence of energy barriers in the entrance channel in all cases. The accuracy of the interpolated 6D PES is checked by comparing the interpolated values with calculated DFT data not included in the interpolation procedure. In Fig. 2(b) we present this comparison for a selected set of configurations showing the high degree of accuracy obtained in the interpolation. For molecules with occupied π molecular orbitals, such as N2 and O2, interpolation over θ and ϕ is usually more complicated. However, as
shown in the examples of Fig. 3, we also obtain a high degree of accuracy in the interpolation over these variables due to our choice of configurations in the interpolation scheme, which includes various molecular orientations at each position over the surface unit cell. As a result of these comparisons, we can conclude that interpolation errors in our PES are small on average ($\leq 50$ meV) for distances above 2.5 Å from the surface and that below this distance they are kept below 100 meV for those configurations that are relevant in the dynamics. In particular, interpolation errors in the energies of the adsorption wells and in the minimum energy barriers to dissociation and adsorption are kept below few tenths of meV.

Since the aim of this paper is to analyze how the reactivity towards $\text{N}_2$ adsorption differs between the Fe/W(110) and Fe(110) surfaces, we describe in the following the more relevant features of the $\text{N}_2$/Fe/W(110) PES by comparing them to those of the $\text{N}_2$/Fe(110) system [20, 21]. A selection of ($r, Z$)-cuts of the $\text{N}_2$/Fe/W(110) PES is shown in Fig. 4. Panels (a) and (b) correspond to configurations for which molecular adsorption sites exist. As detailed elsewhere [20], the fact that these apparent minima in the ($r, Z$) cuts correspond to local minima in the 6D PES has been verified by placing the molecule at these minima and increasing its energy until it is able to escape the well. The first remarkable feature is that $\text{N}_2$ adsorption occurs for the same two configurations that were identified in Fe(110).

The deepest minimum for both surfaces corresponds to the molecule lying parallel to the surface ($\theta = 90^\circ$, $\varphi = 90^\circ$), with its center of mass over the hollow site. For the Fe/W(110) system, in this adsorption well, the molecule is at $Z \sim 1.2$ Å from the surface and with an interatomic distance $r \sim 1.3$ Å (Fig. 4(b)). The interatomic distance $r$ is slightly larger than in Fe(110) ($r \sim 1.2$ Å) [20] and than the interatomic distance of the molecule in vacuum ($r_{eq} = 1.11$ Å). In addition, the $Z$ position is around 0.2 Å closer to the surface in Fe/W(110) than in Fe(110) [20]. The less deeper well (Fig. 4(a)) is found for the molecule staying upright over the top site at $Z \sim 2.4$ Å ($Z \sim 2.5$ Å in Fe(110)) and $r \sim r_{eq}$ (as in Fe(110)) [20, 21]. However, the main difference between the two surfaces regarding the molecular adsorption wells is the value of the adsorption energies. They are considerably larger in the case of the Fe/W(110) surface. For the equilibrium hollow-parallel adsorption well the (interpolated) adsorption energy is $-517$ meV in Fe/W(110) and $-348$ meV in Fe(110) [21]. The difference is even larger in the case of the top-vertical adsorption well, since the adsorption energy amounts to $-479$ meV for the Fe/W(110) surface and only to
−246 meV in the Fe(110) surface [21][33].

The bottom panels (Fig. 4(c) and 4(d)) correspond to two configurations that can lead to dissociation. In Fig. 4(c) the molecule is located on the bridge site, oriented parallel to the surface (θ = 90°), and pointing towards hollow sites (ϕ = 125.26°). This is the configuration that showed the lowest energy barrier to dissociation in Fe(110) (around 1.1 eV). In the case of N₂/Fe/W(110) the energy barrier for this configuration is ∼1.6 eV, i.e., it increases in about 500 meV. Importantly, such an increase is not a common feature of the whole N₂/Fe/W(110) PES and, as a result, the configurations with the lowest barriers to dissociation in Fe(110) and in Fe/W(110) differ. For Fe/W(110), it corresponds to the configuration of Fig. 4(d). In this case the molecule is located on a hollow site with the molecular axis parallel to the surface (θ = 90°) and pointing towards bridge sites (ϕ = 54.74°). The value of this minimum energy barrier is ∼1.25 eV, which is also slightly lower than the one obtained for the same configuration in the Fe(110) surface (∼1.3 eV).

In sum, the static analysis of these (r,Z) cuts in comparison with those found for the Fe(110) surface would lead one to expect that: (i) N₂ molecular adsorption probabilities on the Fe/W(110) surface will be larger than on the Fe(110) surface (because of the larger molecular adsorption energies) and (ii) Fe/W(110) will be less reactive towards N₂ dissociative adsorption than the Fe(110) surface (larger energy barriers). Nevertheless, a conclusion only based on the analysis of 2D cuts of the PES is often misleading: the molecular initial configuration can be continuously altered along the trajectory due to its interaction with the surface. For this reason, the dynamics of the interaction of N₂ molecules with the Fe/W(110) surface is studied in the following section.

III. ADSORPTION DYNAMICS OF N₂ ON Fe/W(110)

The adsorption dynamics of N₂ on Fe/W(110) is treated classically and neglecting the N₂ zero point energy. The precalculated 6D PES is used to obtain at each integration step the adiabatic force acting on each nitrogen atom. Dynamics simulations are performed following two different schemes: (i) the Born-Oppenheimer static surface (BOSS) approximation, which provides a pure 6D adiabatic dynamics, and (ii) the generalized Langevin oscillator (GLO) model [34, 35], which allows to incorporate energy exchange and surface temperature effects still using the 6D PES. Briefly, the GLO describes surface motion in terms of a 3D
harmonic oscillator where the mass associated with the surface oscillators is the Fe atomic mass $m_{\text{Fe}}$. Dissipation and thermal fluctuations are included through the second fluctuation-dissipation theorem with the help of a ghost 3D oscillator that represents the “thermal bath” that the bulk provides. The same values are used for the surface oscillator frequencies and for the frequencies associated to the ghost oscillators $\omega_{i,x} = 5.6 \times 10^{-4}$ a.u. (atomic units) $\omega_{i,y} = 6.1 \times 10^{-4}$ a.u. and $\omega_{i,z} = 7.6 \times 10^{-4}$ a.u. ($i = 1,2,3$) [36]. The friction coefficients of the ghost oscillators are obtained from the Debye frequency as prescribed in ref. 34.

The BOSS dynamics provides direct and meaningful information on energy barrier distributions and on the configurational space relevant for reactivity. This kind of information is more difficult to disentangle if energy loss processes are included in the dynamics. For this reason, our study of the dissociative adsorption (Section III A) is mainly based on the BOSS method. However, the non-dissociative $N_2$ molecular adsorption requires the molecule to dissipate part of its energy in order to be accommodated in the adsorption well. For this reason, this process is studied in Section III B within the GLO model that accounts for energy exchange between the molecule and the lattice in the dynamics simulation.

In both methods, the adsorption probabilities are obtained for each incidence kinetic energy $E_i$ and incidence polar angle $\Theta_i$ by running a large set of trajectories. This set is generated through a conventional Monte Carlo procedure that samples the initial position over the surface unit cell ($X,Y$) and the molecular orientation ($\theta,\varphi$). All trajectories start with $N_2$ at its (gas-phase) equilibrium bond length $r_{\text{eq}}$ and at $Z=6$ Å. The latter are the conditions that define the reference zero energy of the $N_2$/Fe/W(110) PES (see Section II). In the GLO simulations, an additional Monte Carlo sampling over the position and velocity of the surface and ghost oscillators is performed. As outcomes of the trajectory calculations the following events are distinguished in the BOSS and GLO simulations: (i) dissociation, if the internuclear distance of the molecule reaches $2r_{\text{eq}}$ (i.e. $r > 2.22$ Å) with a positive radial velocity, and (ii) reflection, if the molecular center of mass, after being scattered off the surface, reaches the starting point $Z = 6$ Å with a positive $Z$ velocity. Molecular adsorption is an additional outcome that can only be observed in the GLO dynamics simulations, as explained above. This event is here identified with a molecule that has neither reflected nor dissociated after 30 ps and it has a negative total (kinetic plus potential) energy. The latter condition guarantees that the molecule is already well accommodated in one of the molecular adsorption wells.
A. Dissociative adsorption dynamics

We start by studying the dissociative adsorption process using the BOSS approach for the reasons given above. Figure 5 shows the results for the initial dissociative sticking probability $S_0$ (i.e., the dissociation probability at zero coverage) as a function of the $N_2$ incident energy $E_i$, for different incidence angles $\Theta_i$. Each value $S_0(\Theta_i, E_i)$ is obtained from the evaluation of a minimum of 50,000 trajectories. The first important feature we observe is that dissociation is an activated process with a rather high activation energy. In particular, no sticking event is found below 1.3 eV under normal incidence conditions. This means that the sticking probability is smaller than $2 \times 10^{-5}$. The activation energy provided by the dynamics calculations almost coincides with the energy barrier of 1.25 eV observed in the 2D cuts of the PES (Fig. 4(d)). Interestingly, the dissociative sticking probabilities are smaller than the ones obtained in Fe(110) [20, 21], showing that, in this particular system, surface strain is hampering dissociation instead of favoring it (see Fig. 6(a) for the comparison). An exception from this general behavior is observed at the highest considered angle of incidence (60°) and at 45° angle of incidence in the high energy range. This is not related to the high energy barriers for dissociation in the exit channel discussed above, but to the presence of lower entrance energy barriers that affect the minimum normal energy required for the dissociating molecule to approach the surface. As discussed below, these entrance barriers are higher in Fe(110) [20] than in Fe/W(110).

An interesting difference between the dissociation dynamics in the two surfaces can be observed by analyzing Fig. 7. This figure shows the evolution of the dissociating molecules along the incoming part of the trajectory. The upper panels show the position of the center of mass of the dissociating molecules over the surface unit cell when the molecules first reach the distance $Z$ indicated on top of each panel. The $\theta$-distributions plotted in the bottom panels provide information on the corresponding polar orientation of the dissociating $N_2$. The results are shown for $E_i = 3.0$ eV and normal incidence. At this energy, which is well above the activation energy for dissociation, the number of dissociating molecules is large enough to ensure a reasonable statistical description of the dissociation dynamics. We observe that $N_2$ dissociates through configurations located over bridge and hollow sites that are predominantly oriented parallel to the surface, although few of them deviate in at most ±30° from the surface plane (see bottom panels). This is consistent with the presence of the
lowest energy barriers for these configurations (see Figs. 4(c) and 4(d)). Remarkably, the results of Fig. 7 contrast with what was observed for Fe(110) at the same incident energy (Fig. 7 in ref. 20). In that surface, the dissociating molecules concentrate around the bridge site and almost no dissociation occurs at the hollow site. In the Fe/W(110) surface, we find that for lower incident energies \( E_i = 2.0 \text{ eV} \) dissociation only occurs on the hollow sites [21]. In sum, the dynamics results confirm the minimum energy barriers to dissociation identified in each surface, namely, the configuration of Fig. 4(d) for Fe/W(110) and the configuration of Fig. 4(c) for Fe(110), and they also evidence the change in the dissociation path caused by the heteroepitaxial strain.

Figure 5 also shows that neither total energy scaling nor normal energy scaling is observed. As in Fe(110) [20], for equal total incident energy \( E_i, S_0 \) increases with normal energy (i.e., decreases with \( \Theta_i \), Fig. 5(a)). Similarly, for equal normal energy \( (E_i \cos^2 \Theta_i) \), \( S_0 \) is larger the higher the total incident energy (i.e., the larger \( \Theta_i \), Fig. 5(b)). As it was the case for the Fe(110) surface, this behavior can be rationalized in terms of the barriers that the molecule has to overcome before dissociating. In order to illustrate the latter, we plot in Fig. 8(a) the dependence of the potential energy along the minimum energy dissociation path (in 2D) on the reaction coordinate \( s \) for the configurations of Figs. 4(c) and 4(d) (the red line indicates the dissociation path in each \((r,Z)\)-cut). The reaction coordinate \( s \) is defined as the distance in the \((r,Z)\) space measured from the position of the minimum energy barrier \((s = 0)\) for each configuration. Interestingly, both configurations (hollow \( \theta = 90^\circ, \varphi = 54.74^\circ \) and bridge \( \theta = 90^\circ, \varphi = 125.26^\circ \)) present approximately the same barrier of around 0.4 eV in the entrance channel. It is important to remark that the value of the entrance barrier is confirmed not only for these two particular configurations but for all the dissociating molecules. This can be easily observed in Fig. 8(b) where the average potential energy probed by the dissociating molecules is represented as a function of the distance to the surface. This plot shows an entrance barrier of \( \sim 0.4 \text{ eV} \) at \( Z \approx 2 - 2.5 \text{ Å} \). At these distances (entrance channel) the dynamics is basically controlled by the normal energy. Therefore, for off-normal incidence conditions such entrance barriers may prevent molecules from dissociating even if their total energy is enough to overcome the higher late barriers. This is the reason why the dissociative sticking decreases when increasing the incidence angle for constant total energy. At the same time, due to the high late energy barriers, for constant normal energy dissociative sticking probability increases with total
energy. Note that on Fe(110), the energy barrier at the entrance channel appears at the same distance from the surface. However the barrier is \( \sim 0.6 \text{ eV} \) [20], i.e., 200 meV higher than on Fe/W(110).

For completeness, the dissociation probabilities obtained with the GLO model for normal incidence and different surface temperatures \( T_s \) are shown in Fig. 6(b). Compared to the BOSS results, there is a common and similar reduction in \( S_0 \) for all the considered \( T_s \) that can be rationalized as follows. Since the incidence energies at which dissociation can occur \( (E_i > 1.2 \text{ eV}) \) are much larger than the surface thermal energy, there is a dominant energy flow going from the incoming \( \text{N}_2 \) to the surface. As a result, the molecules, which have lost part of their energy, encounter more difficulties in overcoming the large late dissociation barriers. Note that a similar effect is observed when comparing the BOSS and GLO results for \( \text{N}_2 \) dissociation on Fe(110) (dashed lines in Figs. 6(a) and 6(b), respectively). Figure 6(b) also shows that our conclusions regarding the more reactive character of Fe(110) as compared to Fe/W(110) towards \( \text{N}_2 \) dissociation are also valid when energy exchange with the surface is considered.

Next, let us discuss our results for the dissociative adsorption in connection with existing thermal deposition experiments of \( \text{N}_2 \) on thin (110) oriented Fe layers grown on W(110) [1]. Apart from the observation of molecular adsorption on the (tensile) strained Fe monolayer, the authors also reported the presence of dissociated atomic nitrogen on the surface, even at low temperatures \( (T_s > 80 \text{ K}) \). However, the energy barrier that we obtain \( (\sim 1.25 \text{ eV}) \) seems to be too high to explain \( \text{N}_2 \) dissociation at so low temperatures. In this respect, it is worth mentioning that the barrier to dissociation obtained in DFT calculations of around 1.1 eV for the \( \text{N}_2/\text{Fe}(110) \) system [20, 37, 38] is also much larger than the value of 0.27 eV reported by experimentalists [39]. Such a large mismatch, which can hardly be attributed to the inherent limitations of DFT, led the authors to conclude that the measured lower barrier should be related to dissociation at surface steps or imperfections [37]. Our calculations suggest that also in the \( \text{N}_2/\text{Fe}/\text{W}(110) \) system the presence of steps or other surface defects might cause the measured reactivity. Therefore, the picture that emerges when comparing the theoretical and experimental results is the following. Unlike the Fe(110) surface, the strained Fe monolayer on W(110) is very active towards \( \text{N}_2 \) molecular adsorption as we will show in Section III B. This implies efficient molecular adsorption of \( \text{N}_2 \) under thermal deposition on the strained surface even at low temperatures. Despite the similarity of dissociation barriers
in both systems, the observed dissociated atomic nitrogen on the strained surface when increasing the temperature may be due to dissociation at steps/defects of the previously adsorbed molecular species. This would explain the observation of both molecular and atomic nitrogen adsorption on the Fe/W(110) surface and the absence of adsorption on the Fe(110) surface.

B. Molecular adsorption dynamics

The results of our GLO calculations for molecular adsorption under normal incidence conditions ($\Theta_i = 0^\circ$) are depicted in Fig. 9. The molecular adsorption probability is plotted as a function of the incident energy $E_i$ for three different surface temperatures, $T_s = 80$ K, 300 K, and 500 K. We show separately the probabilities for adsorption in each of the two adsorption wells identified in Section II, namely, the top-vertical and the hollow-parallel. The total adsorption probability irrespective of the adsorption well is plotted in the inset for the three temperatures. As a general trend, the adsorption probabilities increase initially with $E_i$ up to a given energy value and then decrease. The initial increase is related to the existence of energy barriers that the molecules have to overcome in order to be adsorbed. The decrease of the adsorption probability at higher incident energies is due to the reduction of the probability to accommodate molecules in the adsorption wells as the initial energy increases. Furthermore, the adsorption probability tends to decrease when increasing $T_s$. The reason is that as $T_s$ increases less energy is dissipated from the molecule to the surface, which reduces the possibility of N$_2$ being trapped and adsorbed on the molecular well. These general trends were also obtained in the case of N$_2$ adsorption on Fe(110) [20].

One remarkable point is that N$_2$ adsorption at low $E_i$ takes place in the top-vertical well instead of taking place in the energetically more favorable hollow-parallel well. The same situation was obtained for N$_2$ adsorption on Fe(110) and, as in that case, it is rationalized in terms of the different energy barriers that the molecules have to overcome to be adsorbed on one or the other well. These results are also consistent with the experimental observations presented in ref. 1. The ARUPS spectra recorded after thermal deposition of N$_2$ showed that the molecules adsorb standing upright on the surface.

Apart from the different adsorption energies discussed in Section II, another important difference between Fe/W(110) and Fe(110) regarding N$_2$ molecular adsorption is the value
of the energy barriers. Our dynamics simulations show that adsorption on the Fe/W(110) surface requires a minimum initial energy $E_i$ of around 50 meV (the minimum barrier for adsorption in the top-vertical well). On the other hand, adsorption in the hollow-parallel well requires at least around 150 meV of initial incidence energy. These barriers are much lower than the ones obtained for the Fe(110) surface (150 meV and 250 meV, respectively) [20, 21]. Remarkably, the present results are consistent with the experimental observations claiming that at low surface temperatures $N_2$ molecules adsorb on the strained Fe/W(110) surface but not on Fe(110) [1].

Yet, for the experimental conditions of ref. 1 in which $N_2$ is thermally deposited at low temperatures ($T_s=80$ K), one may argue that 50 meV is still a too high energy barrier that may prevent $N_2$ adsorption. In this respect, it has been shown that even if the RPBE functional is constructed in order to improve the calculated adsorption energies of molecules such as $N_2$ and $O_2$ in transition metal surfaces [23], it usually provides too high energy barriers at the entrance channel [40]. For this reason, the less repulsive PW91 functional [41] has also been used to compute the potential energy as a function of distance $Z$ from the surface for the top-vertical configuration. In this case, the adsorption process becomes non-activated for the Fe/W(110) surface since no barrier is present in the $E(Z)$ curve. This would imply an efficient adsorption of $N_2$ on the top-vertical site under thermal deposition even at low temperatures, which is consistent with the experimental observations [1]. On the contrary, for the Fe(110) surface even using the PW91 functional the adsorption in the top-vertical well remained activated.

Continuing with the results of Fig. 9, we observe that $N_2$ adsorption is dominated by the top-vertical well up to incidence energies well above the energy barrier of about 150 meV that limits the access to the hollow-parallel well. Noticeably, the adsorption probabilities at 80 K and 300 K are very high. The larger adsorption energies of $N_2$ on the Fe/W(110) surface as compared with the ones obtained on Fe(110), allow us to rationalize the quantitative differences between the absolute values of the molecular adsorption probabilities obtained in each surface. At the lowest simulated surface temperature ($T_s=80$ K), the maximum (total) adsorption probability in Fe/W(110) is around 94% at $E_i=0.45$ eV (see inset). Additionally, among the adsorbed molecules at this energy, around 90% of them are adsorbed on the top-vertical well. However, in the Fe(110) surface the maximum (total) adsorption probability is $\sim 55\%$ and it occurs at a higher incident energy ($E_i=0.75$ eV) [21]. Another remarkable
difference between both surfaces is observed at high incidence energies. For instance, in
the case of Fe/W(110), at the highest calculated energy ($E_i \sim 3.0$ eV) the adsorption
probabilities are similar in the two wells, while for Fe(110) only around 5% of the adsorbed
molecules remain on the top-vertical well for the same incidence energy. The reason is that
the adsorption energies of both wells in the Fe/W(110) surface differ in less than 50 meV,
while the difference is about 100 meV in Fe(110). Thus, the greater similarity in the depth
of the hollow-parallel and the top-vertical wells tends to equalize the probability to populate
each of them. Note that the maximum adsorption probability obtained in the top-vertical
well for Fe(110) amounts to only around 40% [20, 21], whereas for Fe/W(110) more than
80% of molecules can be adsorbed on this site. All in all, the present simulations show that
the experimentally observed enhancement of N$_2$ adsorption on the strained Fe monolayer
under thermal deposition also remains at hyperthermal $E_i$.

IV. COMPARISON BETWEEN Fe/W(110) AND Fe(110): ELECTRONIC AND
TOPOGRAPHICAL CONSIDERATIONS

In an attempt to qualitatively understand the different energetics ruling N$_2$ adsorption
and dissociation between the Fe/W(110) and the Fe(110) surfaces, we apply in this section
the ideas of the $d$-band model proposed by Hammer and Norskøv [13, 14] and we adapt
them to the intrinsic properties of the N$_2$/Fe/W(110) and N$_2$/Fe(110) systems. According
to the original $d$-band model [13], adsorption (dissociation) on transition metal surfaces is
basically controlled by the interaction of the adsorbate states with the surface $d$-band. The
latter is approximated by a single state located at the (energy) center of the band $\varepsilon_d$. In the
case of transition metals, this approach can be justified by the relative narrowness of their
$d$-bands, which originates from the small coupling between the localized $d$-states. As a con-
sequence of the molecule-surface interaction, the adsorbate and metal states hybridize and
split into bonding and antibonding adsorbate-surface states. Following concepts borrowed
from molecular bonding theory, the authors define the *reactivity measure* $\delta E_{TS}$ (see below)
that depends on the energy position of the molecular states respect to the $d$-band center $\varepsilon_d$,
the filling factor of the hybridized molecule-surface states at the adsorption (transition state)
positions, and the coupling matrix element between the molecular orbitals (MOs) and the
(metal) surface $d$-states. As a general trend the adsorption energy and the minimum energy
barrier to dissociation (MEBD) would be linearly correlated with $\delta E_{TS}$. Thus, the smaller the $\delta E_{TS}$ value, the deeper is the adsorption well (the lower the MEBD) [13]. Specifically, Hammer et al. found that the non-activated dissociation of H$_2$ on transition metal surfaces is characterized by $\delta E_{TS} < 0$, while the largest $\delta E_{TS}$ values are obtained for H$_2$ dissociation on the inert Au surfaces [13].

Since the $d$-band model was initially applied for H$_2$ interacting with non-magnetic surfaces, we have adapted it to the particular case of a N$_2$ molecule, for which the MOs to be considered are, in principle, the $\pi_u$ and $\pi^*_g$ MOs, each with four electrons, and the $\sigma_{pz}$ MO, with two electrons. Moreover, due to the magnetic character of the Fe surface (and monolayer), the spin-up and spin-down density of states (DOS) have to be treated separately. Therefore, we calculate the spin-up ($\varepsilon_{d}^{\uparrow}$) and spin-down ($\varepsilon_{d}^{\downarrow}$) $d$-band centers as

$$\varepsilon_{d}^{\uparrow,\downarrow} = \frac{\int_{-\infty}^{\infty} \rho_{d}^{\uparrow,\downarrow}(\varepsilon) \varepsilon \, d\varepsilon}{\int_{-\infty}^{\infty} \rho_{d}^{\uparrow,\downarrow}(\varepsilon) \, d\varepsilon},$$

(1)

where $\rho_{d}^{\uparrow}(\varepsilon)$ ($\rho_{d}^{\downarrow}(\varepsilon)$) is the spin-up (spin-down) site- and $d$-projected density of states (PDOS), i.e., the surface DOS projected onto $d$-orbitals centered at each surface atom. In the present analysis only the $d$-PDOS of the topmost surface layer, which is shown in Fig. 10, has been used to calculate Eq. (1), because only this layer is clearly perturbed upon N$_2$ adsorption. The corresponding $\varepsilon_{d}^{\uparrow,\downarrow}$ values are written in the first two columns of Table I and plotted in Fig. 10 by vertical blue bars.

The filling factors $f_{m}^{\uparrow,\downarrow}$ of the hybridized state between the MO $m$ of N$_2$ and the surface states are estimated from the (spin-resolved) projection of the system’s DOS onto the corresponding $m$-MO of N$_2$ located at the state of interest. More precisely, the $m$-PDOS is defined for each spin state ($s = \uparrow, \downarrow$) as

$$\text{PDOS}_{m,s}(\varepsilon) = \sum_{n,k} |\langle \psi_{m,s,k}^{MO} | \phi_{n,s,k}^{TOT} \rangle|^2 \delta(\varepsilon - \varepsilon_{n,s,k}),$$

(2)

In this expression $\sum_{n,k} \delta(\varepsilon - \varepsilon_{n,s,k})$ is the DOS of all (n,k) states with spin $s$, $\psi_{m,s}^{MO}$ the $m$-MO with spin $s$, and $\phi_{n,s,k}^{TOT}$ the state of the full system, where $n$ and $k$ refer to the band index and $k$-points, respectively. Here, the different PDOS$_{m,s}(\varepsilon)$ are calculated with the implementation of ref. 42 [43]. The value $f_{m}^{s}$ is obtained by integrating the corresponding PDOS$_{m,s}(\varepsilon)$ up to the Fermi energy $E_F$. Since, each $(m,s)$-MO is normalized to one, a value $f_{m}^{s} = 0.5$ is associated to a completely filled hybridized bonding state and a completely empty
hybridized antibonding state, while a value \( f^s_m = 1 \) corresponds to fully occupied bonding and antibonding \( N_2 \)-surface states. In all the cases considered here, the \( \sigma^\uparrow \) and \( \pi^\uparrow \) MOs are all occupied \((f^s_m \approx 1)\). Therefore, the reactivity measure \( \delta E_{TS} \) is only determined by the hybridization of the \( \pi^*_g \) MOs with the surface \( d \)-band states. Its value is calculated as

\[
\delta E_{TS} = \sum_{m=x,y} \left[ -a^\uparrow_m V^2_m \left| \varepsilon^\uparrow_d - \varepsilon^\pi^*_g \right| - a^\downarrow_m V^2_m \left| \varepsilon^\downarrow_d - \varepsilon^\pi^*_g \right| + \alpha_m V^2_m \right].
\]

(3)

The summation in \( m \) is taking into account that there are two \( \pi^*_g \) MOs. Furthermore, \( \varepsilon^\pi^*_g \) denotes the energy of the \( \pi^*_g \) states far from the surface, which are energetically degenerated.

The first two terms in the square bracket describe the energy gain due to the hybridization of the \( \pi^*_g \) MOs with the \( d \)-states for both the spin-up and the spin-down states. The factors \( V^2_m \) represent the coupling matrix elements between each \((m, s)\)-MO and the metal \( d \)-states. Following Hammer et al. the factor \( a^s_m \), which weights the attractive contribution of the bonding and the repulsive contribution of the antibonding hybridized states, is related with the filling factor \( f^s_m \) as: \( a^s_m = 2f^s_m \) for \( f^s_m \leq 0.5 \) and \( a^s_m = 2(1 - f^s_m) \) for \( 0.5 < f^s_m \leq 1 \).

In our case the factor 2 assures that the highest occupation of the bonding and of the antibonding states is one [44]. Finally, the last term in Eq. (3) is repulsive and accounts for the orthogonalization of the \( \pi^*_g \) MOs with the \( d \)-states.

Let us start by comparing the reactivity measure \( \delta E_{TS} \) for molecular adsorption on Fe(110) and Fe/W(110). The orbital-PDOS at the top-vertical and hollow-parallel adsorption sites are shown in Fig. 11 for both surfaces. The results of the reactivity measure are shown in Table I. Note that \( V^2_m \) and \( \alpha_m V^2_m \) have been taken equal on both systems, as they refer to the \( d \) states on the topmost layer of the surface, which in both cases is Fe, and also independent of \( m \) in view of the similar filling factors of \( \pi^*_g,x \) and \( \pi^*_g,y \) \((f_x \approx f_y)\).

Table I shows that the value \( \delta E_{TS} - \alpha V^2 \) for adsorption on the hollow-parallel site is more negative in Fe/W(110) than in Fe(110) \((-4.60 V^2 \text{ eV} \text{ vs. } -2.74 V^2 \text{ eV})\). These results are in agreement with the well being deeper on Fe/W(110) than on Fe(110) \((-517 \text{ meV} \text{ vs. } -348 \text{ meV})\). Similar results are obtained for the top-vertical adsorption well that also agree with the finding that the adsorption energy is larger on Fe/W(110) \((-479 \text{ meV})\) than on Fe(110) \((-246 \text{ meV})\). Interestingly, the \( d \)-band model also predicts a larger adsorption energy for the hollow-parallel well compared to the top-vertical well in both surfaces. Note that, the differences of \( \delta E_{TS} \) between the hollow-parallel and top-vertical adsorption sites in both surfaces are due to the larger filling factors for the \( \pi^*_g-d \) bonding state obtained in
the case of the hollow-parallel adsorption sites. However, the filling factors, which are very similar for the two surfaces, cannot explain the different $\delta E_{TS}$ values obtained in Fe/W(110) and in Fe(110). In this case, the reason is the different energy position of the $\pi_g^*$ MOs respect to the $d$-band center that enters in the denominators in Eq. (3). We observe that the spin-down $\pi_g^*$ states are much closer to the spin-down $d$-band center in the expanded Fe/W(110) surface than in Fe(110). The energy difference between the $\pi_g^*$ states and the spin down $d$-band center is 0.46 eV in the Fe/W(110) surface and 0.79 eV in the Fe(110) surface (see Table I and Fig. 10). In other words, the deeper adsorption wells and the concomitant reduction of the energy barrier in accessing each well on Fe/W(110) are ultimately a consequence of its smaller work function as compared to that of the Fe(110) surface. Note that the reduction of the entrance energy barriers ($Z > 2$ Å) seems to be a common feature of the $N_2$/Fe/W(110) PES and, therefore, also of the dissociating configurations as already discussed in Section IIIA. Nonetheless, the 2D cuts analysis done in Section II shows that dissociation through those configurations is controlled by the larger late energy barriers that appear when the molecule is already elongated close to the surface ($Z < 1.5$ Å). As a result, we find that other factors different from those ruling the molecular adsorption have to be taken into account to understand the differences between Fe/W(110) and Fe(110) towards dissociation.

As discussed in Section II, the changes that the heteroepitaxial surface strain is causing in the dissociation properties are rather involved. On the one hand, the energy barrier increases in about 500 meV on the strained Fe/W(110) surface for the configuration presenting the lowest barrier to dissociation on Fe(110), which corresponds to $N_2$ centered on a bridge site with $\theta = 90^\circ$ and $\varphi = 125.26^\circ$ (see sketch in Fig. 4(c)). On the other hand, the minimum energy barrier for the configuration over hollow depicted in Fig. 4(d) slightly decreases from $\sim 1.3$ eV in Fe(110) to $\sim 1.25$ eV in Fe/W(110). The complexity of these opposite changes seems far beyond the simplicity of the $d$-band model. Indeed, this is what the $\delta E_{TS}$ values calculated for the dissociating configuration over bridge show. In this case, the orbital-PDOS is calculated with the molecule placed on the transition state position corresponding in both cases to $N_2$ centered on a bridge site with $r \sim 1.9$ Å and $\theta = 90^\circ$ and $\varphi = 125.26^\circ$. The corresponding PDOS for the two surfaces is shown in Fig. 12. The results of $\delta E_{TS}$ on both surfaces are shown in Table II. The lower value of $\delta E_{TS} = -2.82 V^2$ eV obtained for Fe/W(110) compared with $-1.60 V^2$ eV for Fe(110) is not in agreement with
the larger barrier of 1.6 eV for the former compared with 1.1 eV for Fe(110). We find that the changes in dissociation are better understood in terms of the differences in the N adsorption properties between the two surfaces as explained next.

N₂ dissociation will occur when the individual N atom-surface attraction becomes greater than the strong N-N interaction. In the case of the dissociating configuration centered on bridge, the N atoms are attracted towards their nearest hollow sites (see sketch of Fig. 4(c)), whereas in the hollow-centered N₂ configuration the N atoms are attracted by the corresponding nearest bridge sites (see Fig. 4(d)). Thus, any change in the atomic PES for the atom located at hollow (bridge) site is expected to affect the late energy barrier of the dissociating configuration over bridge (hollow). With this in mind, we compare in Fig. 13 the interaction energy of a N atom located on the hollow and bridge sites of the Fe(110) and Fe/W(110) surfaces as a function of the distance from the surface. The DFT calculations have been performed with the same settings as in the molecular case. Focusing on the hollow site, we observe that the energy minimum is \( \sim 0.2 \text{ eV} \) higher in Fe/W(110) than in Fe(110). The lower binding on the more open Fe/W(110) surface is a consequence of the \( \sim 0.2 \text{ Å} \) displacement of the minimum towards the surface. The N atom being forced to get closer to the surface feels at the same time the repulsion from the atom in the second layer beneath. Such a repulsion is particularly strong because the latter is a large W atom. Therefore, the observed decrease of the N binding energy at hollow sites in Fe/W(110) explains the observed increase of the minimum energy barrier for the dissociating bridge configuration in Fe/W(110). In contrast, Fig. 13 also shows that when N is over the bridge site, which is the relevant position for N₂ dissociation with the center of mass on the hollow site, the energy difference between the two minima is much smaller (\( \sim 50 \text{ meV} \)). In fact, it is more attractive in the expanded Fe/W(110) surface. This can be reconciled with the similar barriers obtained in the two surfaces along the hollow-centered dissociation path. Increases of dissociation energy barrier heights with strain have been successfully explained by analogous arguments in other systems [6, 45–47].

V. SUMMARY

In summary, we have studied the dynamics of N₂ adsorption in a strained monolayer of Fe grown on top of a W(110) surface performing molecular dynamics calculations in a six-
dimensional DFT PES. By comparing the present results with those obtained in the clean Fe(110) surface [20] we have been able to understand the differences in the reactivity towards \( \text{N}_2 \) adsorption in both surfaces. We have seen that in both systems two molecular adsorption sites exist: one with the molecular axis parallel to the surface and a second one with the molecule oriented vertical to the surface. Although the former corresponds to the equilibrium adsorption well in both cases, the latter is the one that presents the lowest energy barrier and, hence, the one that is populated at low incident energies of the molecule. An enhanced adsorption probability has been observed on Fe/W(110) as compared with Fe(110). The reason for this is twofold. On the one hand, the activation barriers are very much reduced in this system. In fact, considering the uncertainty inherent to a DFT calculation related to the choice of the exchange correlation functional, it cannot be discarded the possibility that adsorption in the top-vertical well is a non activated process in Fe/W(110). On the other hand, the adsorption energy for the top-vertical well is also enhanced in Fe/W(110) compared with Fe(110), which favors the equilibration of the molecules in this well. The maximum adsorption probability in the top-vertical well is around 85% in the Fe/W(110) surface and only 40% in Fe(110). These results explain the experimental observations of Homann et al.[1] regarding the molecular adsorption on these surfaces. More precisely, the fact that under thermal deposition at 80 K the Fe(110) surface is inert towards \( \text{N}_2 \) adsorption whereas the Fe/W(110) is not, can be nicely reconciled with the present results. The lower activation barrier for adsorption on the top-vertical well is also consistent with the recorded ARUPS spectra, which show that the molecule is adsorbed vertical to the surface though the hollow-parallel adsorption well is energetically more favorable. We note that the fact that the adsorption wells in Fe/W(110) are deeper than in Fe(110) is in accordance with the predictions of the \( d \)-band model and is due to the lower work function of the former.

Regarding the dissociation dynamics, the main difference between the two surfaces is the fact that the minimum energy reaction path is different in each case. In the Fe(110) surface, at low energies, the molecules dissociate with their center of mass on the bridge site, parallel to the surface, and with the molecular axis pointing to the hollow sites [20]. However, in Fe/W(110), the minimum barrier to dissociation corresponds to a configuration with the center of mass of the molecule over the hollow site and oriented parallel to the surface with its axis pointing towards the bridge sites. Nevertheless, the energy barriers to dissociation are similar at both surfaces, about 1.1 eV in the Fe(110) surface [20] and about 1.25 eV
in Fe/W(110), although higher for the strained surface. Importantly, this implies that in this system, despite surface strain favors non-dissociative molecular adsorption, it reduces dissociative adsorption. The latter is caused by the excessive stretching of the Fe monolayer that diminishes the efficiency of the N-Fe interaction in promoting dissociation. Noticeably, the obtained energy barrier seems too high to explain the observed atomic nitrogen in the experiments of Homann et. al. \cite{1} under thermal deposition above 80 K. This may suggest that dissociation is occurring at steps and/or surface defects. The need of a previous adsorption of the molecular species before dissociation, forbidden in the experimental conditions for Fe(110) and highly probable in the Fe/W(110), could in this case explain the experimental observation.

VI. ACKNOWLEDGMENTS

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\begin{thebibliography}{9}
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[33] Note that the adsorption energies reported in ref. 20 correspond to the minima of the DFT energy grid and slightly differ from the ones reported here and in ref. 21 that correspond to
minima of the interpolated CRP PES.


[43] In practice, the calculation of the PDOS for a given position of the molecule on the surface involves two steps. Initially, the states of the molecule alone and of the full system need to be calculated. Afterwards, the states of the full system are projected onto the molecular orbitals obtaining the corresponding PDOS.

[44] These relations can be deduced from the following arguments. The hybridized (molecule-surface) bonding state, which is lower in energy than the hybridized (molecule-surface) antibonding state, is the first to be filled and its filling results in an attractive contribution to $\delta E_{TS}$, which is proportional to the bonding occupation. Once the bonding state is completely occupied ($f_m^s > 0.5$), the antibonding state starts to be filled in a factor $2(f_m^s - 0.5)$, which in turn results in a repulsive (positive) contribution to $\delta E_{TS}$. Note that if $f_m^s > 0.5$, the sum of the attractive (negative) bonding and repulsive (positive) antibonding contributions makes $-a_{ij} = -2(0.5) + 2(f_{ij} - 0.5) = -2(1 - f_{ij})$ in Eq. (3).


TABLE I. Values of the different factors contributing to the reactivity measure $\delta E_{TS}$ (see Eq. (3)) for molecular adsorption on the hollow-parallel ($N_{\text{hollow}}^2$) and top-vertical ($N_{\text{top}}^2$) wells that exist in Fe(110) and in Fe/W(110), namely, the spin-up ($\epsilon_{d}^\uparrow$) and spin-down ($\epsilon_{d}^\downarrow$) $d$-band centers of each surface and the filling factors $f_{m}^{\uparrow\downarrow}$ of the $\pi_{g}^*$ MO for each adsorption site and surface. The resulting reactivity measure minus the repulsive term $\alpha V^2$ is given as function of the coupling matrix element $V^2$. The position of the $\pi_{g}^*$ state respect to the Fermi energy is $\epsilon_{\pi_{g}^*}$=1.45 eV for Fe(110) and $\epsilon_{\pi_{g}^*}$=0.89 eV for Fe/W(110). All energies are in eV.

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon_{d}^\uparrow$</th>
<th>$\epsilon_{d}^\downarrow$</th>
<th>$f_{x}^\uparrow$ ($f_{y}^\uparrow$)</th>
<th>$f_{x}^\downarrow$ ($f_{y}^\downarrow$)</th>
<th>$\delta E_{TS} - \alpha V^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{hollow}}^2$/Fe(110)</td>
<td>-1.93</td>
<td>0.66</td>
<td>0.39 (0.32)</td>
<td>0.58 (0.51)</td>
<td>-2.74$V^2$</td>
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<tr>
<td>$N_{\text{hollow}}^2$/Fe/W(110)</td>
<td>-2.02</td>
<td>0.43</td>
<td>0.39 (0.35)</td>
<td>0.56 (0.50)</td>
<td>-4.60$V^2$</td>
</tr>
<tr>
<td>$N_{\text{top}}^2$/Fe(110)</td>
<td>-1.93</td>
<td>0.66</td>
<td>0.19 (0.14)</td>
<td>0.26 (0.22)</td>
<td>-1.42$V^2$</td>
</tr>
<tr>
<td>$N_{\text{top}}^2$/Fe/W(110)</td>
<td>-2.02</td>
<td>0.43</td>
<td>0.15 (0.12)</td>
<td>0.22 (0.19)</td>
<td>-1.96$V^2$</td>
</tr>
</tbody>
</table>

TABLE II. Same as Table I for the $N_2$ molecule located at the position of the barrier to dissociation on the bridge site with $\theta = 90^\circ$ and $\varphi = 125.26^\circ$. All energies are in eV.

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon_{d}^\uparrow$</th>
<th>$\epsilon_{d}^\downarrow$</th>
<th>$f_{x}^\uparrow$ ($f_{y}^\uparrow$)</th>
<th>$f_{x}^\downarrow$ ($f_{y}^\downarrow$)</th>
<th>$\delta E_{TS} - \alpha V^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$/Fe(110)</td>
<td>-1.93</td>
<td>0.66</td>
<td>0.63 (0.66)</td>
<td>0.76 (0.77)</td>
<td>-1.60$V^2$</td>
</tr>
<tr>
<td>$N_2$/Fe/W(110)</td>
<td>-2.02</td>
<td>0.43</td>
<td>0.62 (0.63)</td>
<td>0.72 (0.75)</td>
<td>-2.82$V^2$</td>
</tr>
</tbody>
</table>
FIG. 1. (a) Coordinate system of the N$_2$/Fe/W(110) PES: Fe atoms in orange, W in grey and N$_2$ in blue. (b) Top view of the (1 × 1) Fe/W(110) surface. DFT energy values for the N/Fe/W(110) 3D PES used in the CRP interpolation are calculated for all sites marked by white and black circles. Black circles indicates the (X, Y) position of the configurations used to construct the N$_2$/Fe(110) 6D PES. The shaded area shows the irreducible wedge of the surface unit cell.
FIG. 2. Potential energy of N\textsubscript{2} in front of the Fe/W(110) surface as a function of the distance $Z$, for fixed $X$, $Y$, $r$, $\theta$ and $\varphi$. The calculated DFT points are represented by symbols and the interpolated values by dashed lines. (a) Results obtained for some of the configurations used in the interpolation procedure. In all cases $r = r_{eq}$. (b) Results for various configurations not used as input data in the construction of the interpolated 6D PES. The internuclear distance $r$ is different in each case.
FIG. 3. Comparison between interpolated potential energies (dashed lines) and DFT values not used in the interpolation procedure (symbols): (a) interpolation in $\theta$ and (b) interpolation in $\varphi$ for various positions of the molecule. In all cases $r = r_{eq}$. 
FIG. 4. 2D \((r, Z)\)-cuts of the \(N_2/Fe/W(110)\) PES. Black solid (white dashed) lines correspond to positive (negative) energy values. Thick black solid lines correspond to zero potential energies. The molecular orientation and position over the surface unit cell is schematically depicted in each contour plot. Contour lines separate intervals of 0.2 eV. For the dissociating configurations, the corresponding minimum energy dissociation path is marked in red in (c) and (d).
FIG. 5. Results for the dissociative adsorption of N₂ on Fe/W(110) obtained within the BOSS method: (a) Initial dissociative sticking probability $S_0$ as a function of the initial kinetic energy $E_i$ for different incident angles $\Theta_i$. The inset shows a zoom for $1.25 \leq E_i \leq 2$ eV. (b) Dissociative sticking probability $S_0$ as a function of normal incident kinetic energy.
FIG. 6. Comparison of the N$_2$ initial dissociative adsorption probability $S_0$ on Fe/W(110) (solid lines) and on Fe(110) (dashed lines): (a) $S_0$ as a function of the initial kinetic energy $E_i$ for different incident angles $\Theta_i$ (BOSS calculation). (b) $S_0$ obtained at normal incidence and three surface temperatures $T_s$ with the GLO model.
FIG. 7. Evolution of $N_2$ on the Fe/W(110) surface for 5000 trajectories (BOSS calculation). The incidence conditions are $E_i=3\ \text{eV}$ and $\Theta_i=0^\circ$. Top panels: Position over the unit cell of the molecule center of mass when first reaching a distance $Z$ from the surface. The dissociating and reflecting molecules are plotted in red and grey circles, respectively. On top of each panel, $N_z$ is the fraction of dissociating molecules reaching $Z$ (note that $S_0 = 0.28$). The total percentage of molecules at each $Z$ is indicated in parenthesis. Bottom panels: Associated normalized $\theta$-distribution of the dissociating molecules.
FIG. 8. (a) Potential energy of N₂ interacting with Fe/W(110) as a function of the reaction coordinate s (see text). Negative (positive) s-values correspond to points reached by the incoming molecule before (after) the transition state. The points used to obtain the potential energy curve are marked with full circles in Figs. 4(c) and 4(d). (b) Average value of the potential energy probed by the dissociating molecules at different distances Z under normal incidence and Eᵢ = 3 eV. The error bars indicate the RMSD of the average of the potential energy at each distance Z. When comparing panels (a) and (b) note that the large Z values correspond to the most negative s values.
FIG. 9. Molecular adsorption probability of N$_2$ on Fe/W(110) in the top-vertical (solid lines) and the hollow-parallel (dashed lines) wells as a function of $E_i$, for different temperatures and normal incidence. The total molecular adsorption probability is shown in the inset.
FIG. 10. PDOS calculated for N\textsubscript{2} located at $Z = 5.5$ Å, where the molecule-surface interaction is negligible. Dark blue curves: spin-up and spin-down $d$-PDOS of the surface topmost layer: (a) Fe(110) and (b) Fe/W(110). The corresponding $d$-band center is marked with a vertical bar. The position of the $\pi_u$, $\sigma_{pz}$ and $\pi^*_g$ MOs are shown in green.
FIG. 11. Cyan and brown curves represent the PDOS onto the $\pi_g^*$ molecular orbitals of N$_2$ located at different adsorption sites (note that they are multiplied by a factor 5 for clarity). The dark blue curves show the $d$-PDOS of the surface topmost layer: (a) Fe(110) surface and N$_2$ on the hollow-parallel well, (b) Fe/W(110) surface and N$_2$ on the hollow-parallel well, (c) Fe(110) surface and N$_2$ on the top-vertical well, (d) Fe/W(110) surface and N$_2$ on the top-vertical well.
FIG. 12. Same as Fig. 11 for $\text{N}_2$ at the position of the energy barrier to dissociation for the bridge configuration ($\theta = 90^\circ, \phi = 125.26^\circ$): (a) Fe(110) and (b) Fe/W(110).
FIG. 13. Potential energy of a N atom over Fe/W(110) (solid lines and full symbols) and Fe(110) (dashed lines and empty symbols) as a function of the distance to the surface $Z$. Results are shown for the atom over the hollow site (circles) and the bridge site (squares).