

SURFACE SCIENCE LETTERS

TIGHT-BINDING APPROACH TO FIELD DESORPTION: N₂ ON Fe(111)

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We present a tight-binding cluster calculation including interatomic Coulomb repulsion for field-induced adsorption and desorption. For electric field strengths F up to the desorption threshold $F \sim 1.5$ V/Å for N₂ on Fe(111) we calculate total potential energy surfaces. The variation of the Schottky barrier and of the N₂ vibrational frequency is extracted as a function of F .

The removal of ions of atoms or molecules from surface sites due to the action of electrostatic fields is known as field desorption. It was first observed by Müller [1] and later on investigated by many authors (for early work refs. [2,3] and summary refs [4,5]).

From a mechanistic point of view, field desorption and field evaporation are related processes, involving adsorbed or lattice particles, respectively. Theoretical discussions considered the image hump model [1,2] and the charge exchange model [6,7]. In recent years, a two-stage mechanism (postionization) was derived from experimental data [8] and models were developed to account for the high charge states of ions.

The model potentials for tunneling have been either a simple triangular potential barrier [8] or three-dimensional tunneling potentials [9] or those involving an appropriate value of the effective charge number of ions [10,11] or a model potential involving image terms for the potential energy of tunneling electrons [12]. In a recent paper, bonding distances and vibration frequencies have been considered [13].

All these theories of the field desorption process are phenomenological in nature in that they assume a simple, analytical form for the potential energy seen by an electron. Calculating the transmission probability for an electron to

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tunnel through the potential barrier between an adparticle and the metal they can compute the ionization probability as a function of the distance of the adparticle from the surface and the applied electric field with a few parameters fitted to experimental data. Lacking a microscopic foundation, the phenomenological potential energy curves do not account for charge redistribution and the hybridization changes in the applied electric field. Also the potential energy curves for the adsorbed molecules (or ions) are modeled phenomenologically with arguments based on electrostatics. A microscopic approach based on the linear response approximation of the density functional formalism has been employed by Kahn and Ying [14] to calculate the initial electric field and critical distance for field-induced desorption of rare gas atoms from a tungsten surface. In this approach the critical field is associated with a vanishing Schottky barrier. No statements are made about ionization (i.e. tunneling) probabilities.

In this letter we present a tight-binding cluster calculation for field-induced adsorption and desorption of N_2 on Fe(111). On the open Fe(111) surface we choose a linear adsorption geometry on the topmost Fe atoms, which are sites with highest field strength, the field being normal to the surface. The linear form seems plausible since in the field free case N_2 chooses this position [15,16] on Fe(111) at low temperature. We approximate the substrate by an Fe_4 cluster consisting of one top layer Fe atom and its 3 nearest neighbours in the second layer, hence conserving the local C_{3v} adsorption symmetry (see insert in fig. 1). It has been shown [16] that including more substrate atoms has no appreciable effect on the energy surfaces in the field-free case. The total spin of the Fe cluster has been fixed to $S = 0$; higher spin clusters will be studied in the future.

The tight-binding Hamiltonian as used in the ASED (Atom Superposition and Electron Delocalization) scheme [17] reads

$$H = \sum_{i,\alpha} \epsilon_i^\alpha |\varphi_i^\alpha\rangle \langle \varphi_i^\alpha| + \sum'_{\substack{i,j \\ \alpha,\beta}} t_{ij}^{\alpha\beta} |\varphi_i^\alpha\rangle \langle \varphi_j^\beta| \\ - \sum_{\alpha < \beta} Z_\beta \int \rho_\alpha(\mathbf{r}) |\mathbf{R}_\beta - \mathbf{r}|^{-1} d\mathbf{r} - eF \sum_{\text{adsorbate } \alpha} Z_\alpha |\mathbf{R}_\alpha| \cos \theta, \quad (1)$$

where α and β enumerate the nuclei of charge $(Z_\alpha e)$ at positions $\mathbf{R}_\alpha = (x_\alpha, y_\alpha, z_\alpha)$, and i and j denote the electron eigenstates in the free atoms. θ is the angle between the N_2 axis and the surface normal. The third sum represents the pair-wise repulsion between a nucleus β and the total electronic and nuclear charge density $\rho_\alpha(\mathbf{r})$ at atom α and the last sum shows the field effect on the ions. In the presence of an electric field F the energy eigenvalues on the nitrogens are shifted

$$\epsilon_i^\alpha(F) = \epsilon_i^\alpha(F=0) + eF |\mathbf{R}_\alpha| \cos \theta, \quad (2)$$

and the hopping integrals change as

$$t_{ij}^{\alpha\beta}(F) = t_{ij}^{\alpha\beta}(F=0) + eF \int \varphi_i^{\alpha*}(\mathbf{r}) (z - z_\alpha) \varphi_j^\beta(\mathbf{r}) d\mathbf{r}. \quad (3)$$

The Slater exponents in the (field-free) atomic orbitals ψ_i^α and the electronic energy levels ε_i^α are given in table 1. We have chosen the N exponents to yield good gas phase N_2 properties; this causes the Fe-N band lengths to be a bit

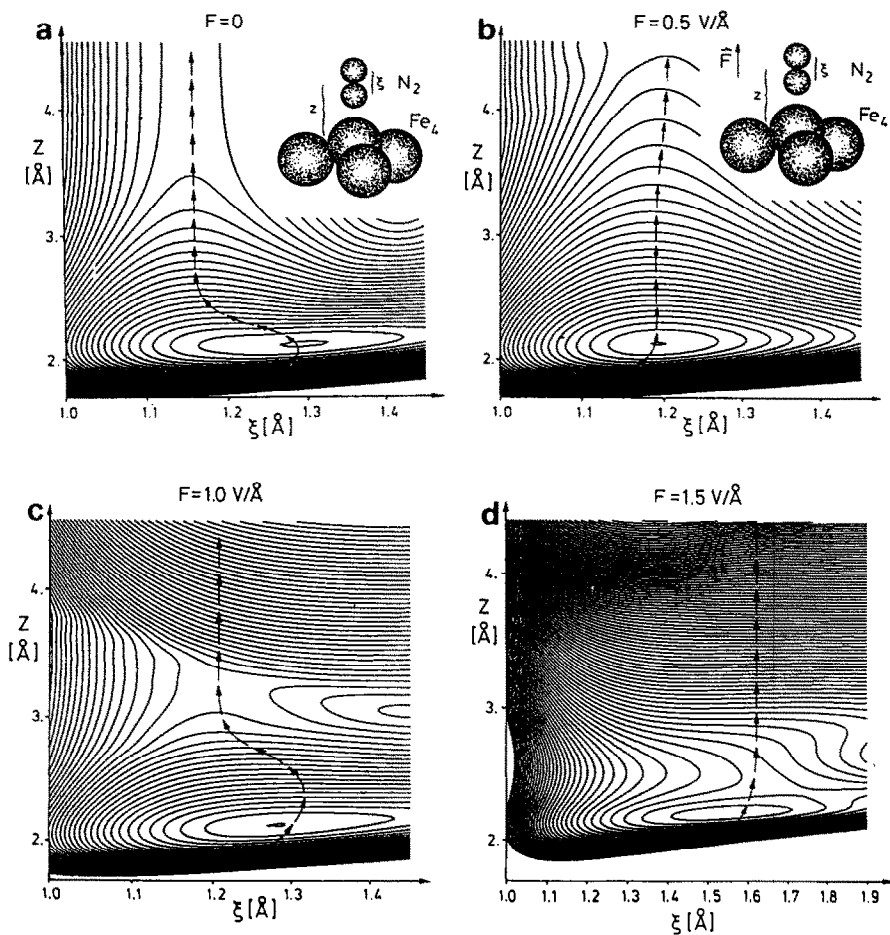


Fig. 1. Potential energy contour plots for the N_2 adsorption on Fe(111) in the presence of an electric field F . z is the height of the N_2 centre of gravity above the topmost Fe atom and ξ the intramolecular distance of N_2 . The assumed field strengths are $F = 0 \text{ V/\AA}$ (fig. 1a), $F = 0.5 \text{ V/\AA}$ (fig. 1b), $F = 1.0 \text{ V/\AA}$ (fig. 1c) and $F = 1.5 \text{ V/\AA}$ (fig. 1d). The equi-distant contours are separated by 0.2 eV. The preferential desorption path is marked by arrows. The insert shows the cluster geometry.

Table 1

Atomic parameters used in the calculation: principal quantum number (n), atomic levels (ϵ) and orbital exponents (ξ); double-zeta Slater basis (with orbital coefficients C) has been used for the levels of Fe

Atoms	s			p		
	n	ϵ (eV)	ξ	n	ϵ (eV)	ξ
Fe ^{a)}	4	-9.37	1.70	4	-5.83	1.40
N ^{b)}	2	-17.83	2.02	2	-12.03	2.02 _{C2}
Atoms	d					
	n	ϵ (eV)	ξ_1	ξ_2	C_1	
Fe ^{a)}	3	-10.50	5.35	1.80	0.547	0.668

^{a)} Ref. [20]; paramagnetic Fe.

^{b)} 2 eV atomic level increase and 0.1 increase in exponents applied to parameters from ref. [21].

short. The field-free hopping integrals are approximated by the Wolfsberg–Helmholtz [18] formula

$$t_{ij}^{\alpha\beta}(F=0) = \frac{1}{2} K_{\alpha\beta} (\epsilon_i^\alpha + \epsilon_j^\beta) \langle \varphi_i^\alpha | \varphi_j^\beta \rangle, \quad (4)$$

where $K_{\alpha\beta} = 2.25 \exp(-0.13 \text{ \AA}^{-1} |\mathbf{R}_\alpha - \mathbf{R}_\beta|)$. Because the atomic orbitals φ_i^α are non-orthogonal, we cannot account for the atomic polarization effects in (3) but only include field effects with the energy shift in (2).

In our calculation we keep the geometry of the Fe₄ cluster fixed and vary the nitrogen positions for a field F perpendicular to the surface ($\theta = 0$) to calculate the potential energy surfaces $V(z, \xi)$. Here, z is the centre of mass position with respect to the topmost Fe and ξ is the intermolecular distance of the N₂ cluster.

In fig. 1 we present potential surfaces of N₂ interacting with Fe(111) plotted as contour maps. Fig. 1a represents the field-free case. We see that in the adsorption minimum the N–N distance ξ has been widened from the value in the gas phase $\xi_0 = 1.1 \text{ \AA}$ to approximately $\xi = 1.2 \text{ \AA}$. The centre of mass of N₂ is at about $z = 2.13 \text{ \AA}$ above the topmost Fe. We should note that the charge on the inner N is $Q \approx +0.4e$ and on the outer one is about $-0.7e$ as inferred from a (basis-dependent) population analysis. As indicated by a schematic desorption path, the N₂ molecule contracts and stiffens to its gas phase properties at distances larger than about 4 \text{ \AA} above the surface. Applying a field $F = 0.5 \text{ V/\AA}$ (fig. 1b) the highest occupied N₂ orbitals of antibonding character are lifted beyond E_F and drained of electrons, causing the adsorbed N₂ molecule to contract and to stiffen already in its equilibrium position. In a field $F = 1.0 \text{ V/\AA}$ (fig. 1c) further large upward shift of adsorbate orbitals, accompanied by N₂-bonding orbitals, and the concurrent reduction in the

hopping strength lead to an expansion and softening of the N_2 bond. Adiabatic desorption now leads the N_2 molecule through an energy maximum at $z \sim 2.5 \text{ \AA}$ beyond which the N_2 is accelerated away from the surface and dissociated. The latter is caused by the fact that by now the bonding orbitals of N_2 have been lifted beyond the Fermi energy E_F and thus drained of electrons. It is worth noting that this phenomenon is a feature of a ground state calculation. As long as we are only interested in equilibrium properties, we allow the total system to relax to its electronic state of minimum energy; this, e.g., implies that beyond the energy barrier the nitrogens are accelerated away to infinity losing all electrons to the substrate. In practice this will not happen due to the low tunneling probabilities from the N's to the substrate. To determine the ion yield in field desorption one therefore has to know both the energy surfaces and the tunneling probabilities (the latter as a function of distance).

In a field $F = 1.5 \text{ V/\AA}$ (fig. 1d) we find that the nitrogen molecule is stretched to $\xi \approx 1.5 \text{ \AA}$ and the N's carry charges $+2e$. The Schottky barrier has been reduced substantially suggesting that – by ground state arguments alone – the critical electric field necessary for desorption is somewhat larger than 1.5 V/\AA . This easy dissociation is a direct consequence of the fact that our one-electron calculation does not include intra-molecular Coulomb repulsion in the formation of ions which e.g. leads only to charge states $+2e$, $+4e$, ... for the desorbed N_2 complex.

In fig. 2 we have plotted the potential energy along the desorption paths marked by arrows in fig. 1. For weak fields the energy surfaces are shifted upwards as a result of the shift in the adsorbate orbitals. In stronger fields ($F \geq 1 \text{ V/\AA}$) these orbitals are raised above E_F and drained of electrons causing the total energy of the system to decrease again. The binding energy of the adsorbed molecule, i.e. the energy difference between the minimum and the top of the Schottky barrier, increases in weak fields leading to field-enhanced adsorption as found experimentally. For the larger fields the Schottky barrier is reduced and moves closer to the surface. In these model calculations field desorption occurs beyond field strengths $F_{\text{crit}} > 1.5 \text{ V/\AA}$ for which the Schottky barrier disappears. This magnitude of field strength has also been observed experimentally. In a recent investigation in the pulsed-laser imaging atom probe Ai and Tsong [19] could detect field desorbed N_2^+ ions from Fe surfaces when field strength values of $F \geq 1.4 \text{ V/\AA}$ were applied.

As indicated above, equilibrium calculations, as presented here, lead to higher and higher charge states as the molecule moves away from the surface in an electric field. This is reflected in the slopes beyond the Schottky barrier. For fields $F = 1 \text{ V/\AA}$ and $F = 1.5 \text{ V/\AA}$ it corresponds an initial charge $+6e$, and at large distances from the surface all valence electrons are removed from the nitrogen atoms. Such effects are, of course, absent in phenomenological models [1–13].

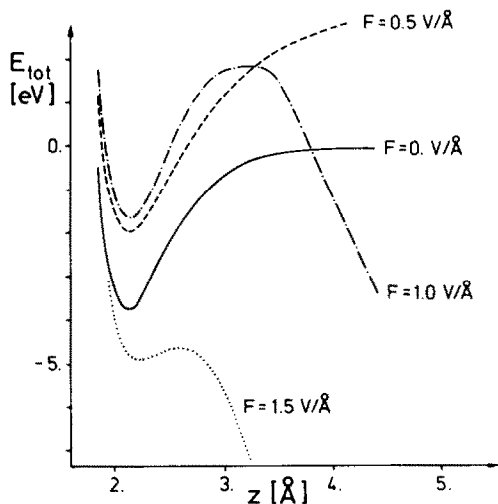


Fig. 2. Potential energy E_{tot} of N_2 molecules desorbing from Fe(111) along the arrows plotted in fig. 1 in absence and in presence of applied electric fields F . (Energy given with respect to the desorbed N_2 in the field-free case.)

From the potential energy surfaces of fig. 1 we can also calculate the field dependence of the N_2 vibrational frequency ν as plotted in fig. 3. In the absence of a field, the vibration in the adsorbed molecule is reduced from its

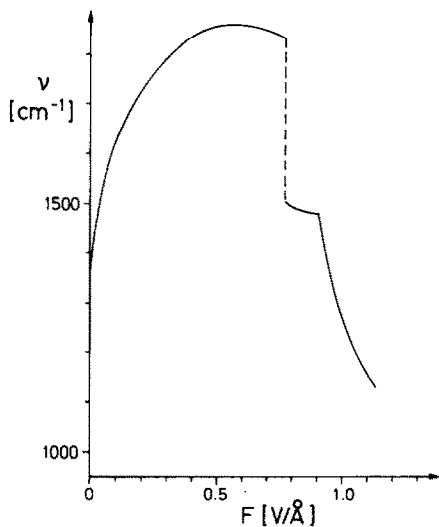


Fig. 3. N_2 vibration frequency ν as a function of the applied electric field F .

gas phase value $\nu_0 = 2359 \text{ cm}^{-1}$ to $\nu(F=0) = 1339 \text{ cm}^{-1}$ mainly due to a partial occupation of N_2 antibonding orbitals. The amount of the frequency softening is caused by the N_2 interaction with the reactive iron (half filled d-band) at a site with the most unsaturated bonds. For fields less than 0.5 V/\AA ν increases again up to a value of about 1850 cm^{-1} due to the fact that the anti-bonding orbitals in N_2 are drained. The abrupt decrease in ν at $F \geq 0.75 \text{ V/\AA}$ is accompanied by an abrupt widening of the N-N distance and a decrease in the N_2 force constant. At this value of F group orbitals which were partially localized on N_2 have been drained leaving the N_2 molecule with a bonding orbital occupation decreased by $0.3e$. The dramatic decrease in ν beyond $F \sim 0.9 \text{ V/\AA}$ is indicative of field-induced dissociation.

As indicated above, potential energy curves alone are not sufficient to describe the field desorption mechanism. What is needed in addition is the probability for an electron localized on the adsorbate to tunnel through the potential barrier $\phi(\mathbf{r})$ by which it is separated from the substrate. The latter can be calculated from the total charge distribution $\rho(\mathbf{r})$ as

$$\phi(\mathbf{r}) = -e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + eFr \cos \theta \Theta(r \cos \theta), \quad (5)$$

where the unit step function Θ accounts for the absence of an electric field in the metal. We will present such a calculation in the near future. The present calculation will also be improved by including atomic polarization in (3).

In summary, we have developed a microscopic approach to field desorption employing a tight-binding cluster calculation. We find field-enhanced adsorption in weak electric fields. From the total potential energy surfaces we can extract the shape of the Schottky barrier and determine the desorption field strength. We further predict the field dependence of the internal vibration of the adsorbed molecule.

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