

THEORETICAL APPROACH TO FIELD DESORPTION, TIGHT BINDING CALCULATION OF N_2 ON Fe(111)

D. TOMANEK, H.J. KREUZER* and J.H. BLOCK*

*Inst. f. Theoretische Physik, F.U. Berlin, Arnimallee 14,
D-1000 Berlin 33, F.R.G.*** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-1000 Berlin 33, F.R.G.*

Résumé - Nous avons développé une approche microscopique de la désorption de N_2 en employant un calcul de liaisons d'agrégats basé le principe de superposition atomique et de délocalisation des électrons, comme il a été développé par A.B. Anderson. Pour de faibles champs électrique, l'accroissement d'adsorption du N_2 au champ est calculé pour une géométrie linéaire d'adsorption vers un atome de Fe du plan (111), était approximée par un agrégat Fe_4 . A partir de l'énergie potentielle totale de surface, nous pouvons extraire la forme de la barrière de Schottky et déterminer la force de champ de désorption. La dépendance en champ de la vibration interne de la molécule adsorbée est prédite et donne, avec des champs croissants, d'abord une contraction puis une extension de la longueur de la liaison N-N.

Abstract - We have developed a microscopic approach to field desorption, employing a tight-binding cluster calculation based on the atomic superposition and electron delocalization scheme as developed by A.B. Anderson. At weak electric fields the field-enhanced adsorption is calculated for a linear adsorption geometry on a topmost Fe atom of a (111) surface, approximated by an Fe_4 -cluster. From the total potential energy surfaces we can extract the shape of the Schottky barrier and determine the desorption field strength. The field dependence of the internal vibration of the adsorbed molecule is predicted which results, with increasing field strength, first in a contraction and then in an extension of the N-N bond length.

I - INTRODUCTION

The phenomenon of field desorption, first observed by E.W. Müller, has since then been investigated by many authors. Theoretical discussions considered the image hump model /1,2/, the charge exchange model /3,4/ and a two-stage mechanism, i.e. the post-ionization process /5/. The model potentials for tunneling have been either a simple triangular potential barrier /5/ or a three-dimensional tunneling potential /6/. An appropriate value of the effective charge number of ions has been introduced by other authors /7,8/ or image terms for the potential energy of tunneling electrons have been involved /9/. From the field evaporation data bonding distances and

*Permanent address : Dept. of Physics, Dalhousie University, Halifax, Nova Scotia, Canada

vibration frequencies of surface atoms have been considered /10,11/.

All these theories of field desorption or field evaporation processes are phenomenological in nature and assume a simple analytical form for the potential energy which acts on the tunneling electron. These phenomenological potential energy descriptions do not account for charge redistributions and the hybridization changes in the applied electrostatic field.

In this contribution a tight-binding cluster calculation is presented for the field-induced adsorption and desorption of N_2 on Fe(111). In our model, a linear adsorption geometry of N_2 on the topmost Fe atoms is chosen. The linear form seems plausible since in the field free case N_2 has this position on Fe(111) at low temperatures /12,13/. 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 (Fig. 1). It has been shown by Tomanek and Bennemann /13/ that including more Fe-substrate atoms (up to twelve) has no remarkable effect on the energy surface in the field free case.

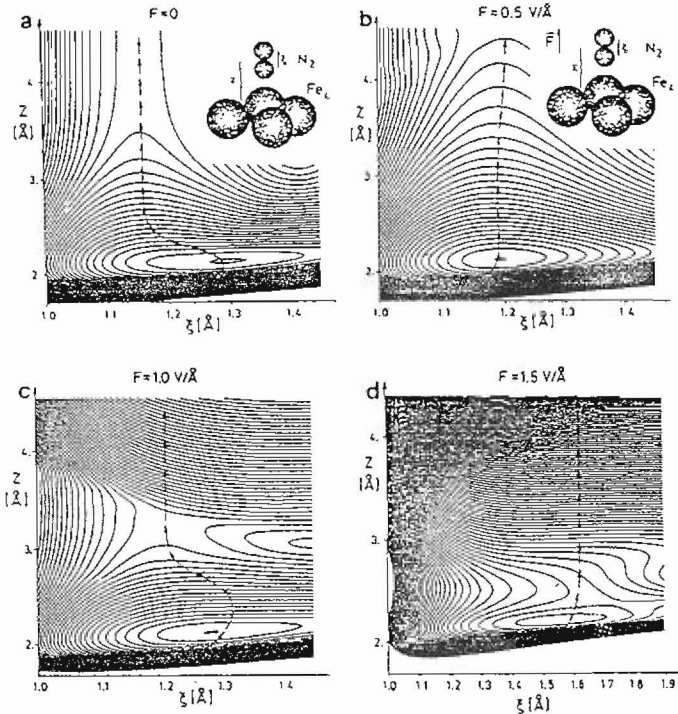


Fig. 1 - Potential energies for $N_2/Fe(111)$ in presence of electrostatic fields F . The equi-distant contours are separated by 0.2 eV, the preferential desorption path is marked by an arrow.

The cluster calculation follows the formalism which was developed by Alfred B. Anderson /14/ and is called ASED = Atomic Superposition and Electron Delocalization.

It is an extended Hückel method which is adding a two-body repulsive energy, taking the Hellmann Feynman theorem into account (validity of classical electrostatics). This method has been proven to predict fairly well the bond length and force constant data of diatomic molecules /14/ and has recently been applied with success to predict properties of chemisorbed molecules /15/, i.e. CO on Pt (111) in the presence of potassium.

The tight-binding Hamiltonian as used in the ASED scheme /14/ reads

$$\begin{aligned}
 H = & \sum_{i,\alpha} \epsilon_i^\alpha |\varphi_i^\alpha\rangle \langle \varphi_i^\alpha| + \sum_{\substack{i,j \\ \alpha,\beta}} t_{ij}^{\alpha\beta} |\varphi_i^\alpha\rangle \langle \varphi_j^\beta| \\
 & - \sum_{\alpha < \beta} Z_\beta \int P_\alpha(r) |R_\beta - r|^{-1} dr \\
 & - eF \sum_{\text{adsorbate } \alpha} Z_\alpha |R_\alpha| \cos \theta,
 \end{aligned}
 \tag{1}$$

where α and β enumerate the nuclei of charge ($Z_\alpha e$) at positions $R_\alpha = (x_\alpha, y_\alpha, z_\alpha)$ and i and j denote the electron eigenstates in the free atoms. θ is the angle between the N_z 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 $\rho_\alpha(r)$ 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

$$\epsilon_i^\alpha(F) = \epsilon_i^\alpha(F=0) + eF |R_\alpha| \cos \theta,
 \tag{2}$$

and the hopping integrals change as

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 d 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. /17/; paramagnetic Fe.

b) 2 eV atomic level increase and 0.1 increase in exponents applied to parameters from ref. /18/.

$$t_{ij}^{\alpha\beta}(F) = t_{ij}^{\alpha\beta}(F=0) + eF \int_{z-z_\alpha}^{\vec{dr}} \varphi_i^\alpha(r) \varphi_j^\beta(r) dr. \quad (3)$$

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 bond lengths to be a bit short. The field-free hopping integrals are approximated by the Wolfsberg-Helmholtz /16/ 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 $K_{\alpha\beta} = 2.25 \exp(-0.13 \text{ \AA}^{-1} |R_\alpha - R_\beta|)$. 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 Fe_4 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 intramolecular distance of the N_2 cluster.

In Fig. 1 we present potential surfaces of N_2 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 N_2 is at about $z = 2.13 \text{ \AA}$ above the topmost Fe. We should note that the charge on the inner N is $Q \approx +0.4 e$ and on the outer one is about $-0.7 e$ as inferred from a (basis-dependent) population analysis. As indicated by a schematic desorption path, the N_2 molecule contracts and stiffens to its gas phase properties at distances larger than about 4 \AA above the surface. Applying a field $F = 0.5 \text{ V/\AA}$ (Fig. 1b) the highest occupied N_2 orbitals of antibonding character are lifted beyond E_F and drained of electrons, causing the adsorbed N_2 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, 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 $\approx 1.5 \text{ \AA}$ 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

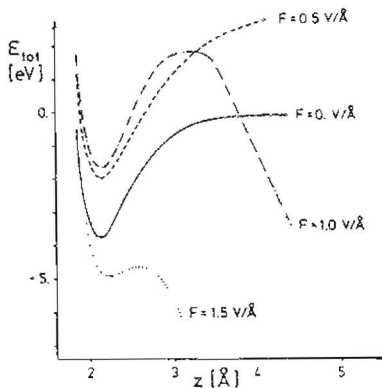


Fig. 2 - Potential energy E_{tot} of N_2 molecules desorbing from Fe(111) along the arrows plotted in Fig. 1 in absence of applied electric fields F . (Energy given with respect to the desorbed N_2 in the field-free case.)

tion is a direct consequence of the fact that our one-electron calculation does not include intra-atomic Coulomb repulsion in the formation of ions which e.g. leads only to charge states $+2e$, $+4e$, ... for the desorbed N_2 complex.

Fig. 2 we have plotted the potential energy along the desorption paths marked by arrows in Fig. 1. For weak fields energy surfaces are shifted upwards as a result of the shift in the adsorbate orbitals. In stronger fields ($F \gtrsim 1 \text{ V/\AA}$) 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.

From the potential energy surfaces of Fig. 1 we can also calculate the field dependence of the N_2 vibrational frequency ν . In the absence of a field, the vibration in the adsorbed molecule is reduced from its 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 $F \gtrsim 0.75 \text{ V/\AA}$ 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 0.3 e. The dramatic decrease in ν beyond $F \sim 0.9 \text{ V/\AA}$ is indicative of field-induced dissociation.

Recent calculations concerned rare gases He, Ne, Ar on W(111) surfaces. It was found that the field induced binding energy of He increased from 5 meV to $\approx 500 \text{ meV}$ at 5 V/\AA due to a charge drain of $\approx 0.3 \text{ e}$. The field binding energy of Ne, on the other hand, increased only slightly with increasing field.

In summary, a microscopic approach to field desorption has been developed 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.

ACKNOWLEDGEMENT

Partial support by the Sonderforschungsbereich Sfb 6/'81 is gratefully acknowledged. We are grateful to A.B. Anderson for providing the ASED programme. One of us (H.J.K.) thanks the Max-Planck-Society for a fellowship.

REFERENCES

- /1/ Müller, E.W., *Naturwissensch.* 29 (1941) 533.
- /2/ Müller, E.W., *Phys. Rev.* 102 (2956) 618.
- /3/ Gomer, R., and Swanson, L.W., *J. Chem. Phys.* 38 (1963) 1613.
- /4/ Tsong, T.T., and Müller, E.W., *Phys. Status Solidi (a)* 1 (1970) 513.
- /5/ Ernst, N., *Surf. Sci.* 87 (1979) 469.
- /6/ Boudreaux, D.S., and Cutler, P.H., *Phys. Rev.* 149 (1966) 170.
- /7/ Haydock, R., and Kingham, D.R., *Surf. Sci.* 104 (1981) L194.
- /8/ Kingham, D.R., *Surf. Sci.* 116 (1982) 273.
- /9/ Ernst, N., and Jentsch, Th., *Phys. Rev.* B24 (1981) 6234.
- /10/ Forbes, R.G., Chibane, K., and Ernst, N., *Surf. Sci.* 141 (1984) 319.
- /11/ Ernst, N., and Block, J.H., *Surf. Sci.* 91 (1980) L27.
- /12/ Grunze, M., Golze, M., Freund, H.J., Pulm, H., Seip, U., Tsai, M.C., Ertl, G., and Küppers, J., *Phys. Rev. Lett.* 53 (1984) 850.
- /13/ Tománek, D., and Bennemann, K.H., *Phys. Rev.* B31 (1985) 2488.
- /14/ Anderson, A.B., *J. Chem. Phys.* 62 (1975) 1187.
- /15/ Ray, N.K., and Anderson, A.B., *Surf. Sci.* 125 (1983) 803.
- /16/ Wolfsberg, M., and Helmholtz, L., *J. Chem. Phys.* 20 (1952) 837.
- /17/ Anderson, A.B., *Surf. Sci.* 105 (1981) 159.
- /18/ Anderson, A.B., Kötz, R., and Yeager, E., *Chem. Phys. Lett.* 82 (1981) 130.