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# A Theoretical Study of the Influence of Surface Structure on Chemisorption of Nitrogen on Iron Single-Crystal Faces

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An Extended Hückel (E. H.) calculation was performed for the energy of $Fe_x$ clusters (with $x = 9, 10, 13, 15, 18$) that are used to model the 111, 100, 110 surface planes of an iron single-crystal. Interaction energies of atomic and molecular nitrogen with each cluster were calculated for different geometrical configurations of the system. From this data thermodynamic and kinetic considerations allowed the following order of reactivity of the different surfaces, in ammonia synthesis, to be estabilished: $111 > 100 > 110$. Comparison with experimental results is more than satisfactory.

## INTRODUCTION

Due to the dramatical influence that ammonia synthesis had on chemical industry and agricultural development, the reaction of formation of ammonia from nitrogen and hydrogen on an iron catalyst has been the object of extensive studies in the last fifty years. A detailed analysis of the earlier work, up to the formulation of a generally accepted mechanism and global rate equation, can be found in a book by A. Nielsen.[1] It is now believed that the assumption that dissociative chemisorption of nitrogen on the metal surface is the rate determining step is essentially correct. In more recent years the influence of the structure of the metal surface on nitrogen adsorption[2] and on the rate of ammonia synthesis[3] has been investigated by means of field emission spectroscopy and kinetic experiments, respectively. No quantum-mechanical studies for this reaction have been reported at our best knowledge, and in the present work the results of a simple E. H. calculation for the dissociation of the $N_2$ molecule on the (111), (100) and (110) planes of an iron single crystal are presented.

## CALCULATIONS

The method of calculation is based on a supermolecular model, made of an appropriate cluster of metal atoms plus the adsorbate, namely a nitrogen molecule or atom, in various locations with respect to the metal surface. The different clusters used to mimic the surface planes are shown in Figure 1. The white and black dots represent atoms on different levels, the cross indicates the adsorption site. The experimental value for the bcc unit cell edge (2.866 Å) was assumed, that corresponds to a nearest neighbour distance of 2.482 Å.[4] $R_{NN}$ is the interatomic distance in $N_2$, $z$ the vertical distance of the
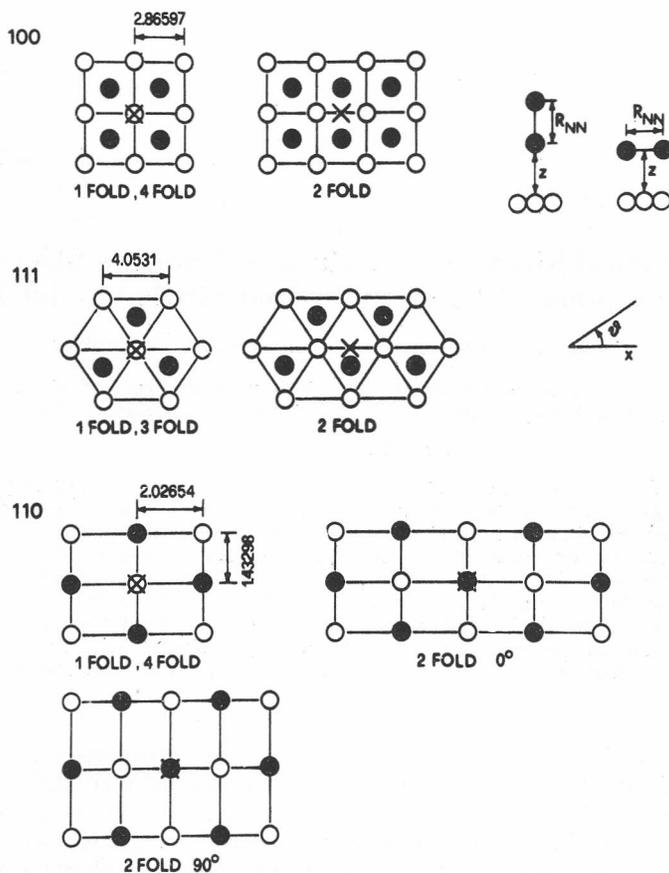
Figure 1. Geometrical parameters ($z$, $R_{NN'}$, $\Theta$) and clusters for the different surface planes. When the same cluster is used to represent different adsorption sites, the white circles belong to the upper level for the 1-fold site, and *vice versa* for the 3- or 4-fold sites.

adsorbate from the upper metal layer, $\Theta$ the angle between the N—N axis (when parallel to the surface) and the $x$ axis. The number of Fe atoms in the cluster ranges from 9 to 18.

TABLE I
*Parameters Used in N and Fe Basis Set*[a]

| Atom | Orbital | V.O.I.P./eV | Exponent | Ref. |
|------|---------|-------------|----------|------|
| N | $2s$ | —26.0 | 1.95 | 6 |
|   | $2p$ | —13.4 | 1.95 | 6 |
| Fe | $3p$ | —66.7 | 4.26 | 7 |
|    | $3d$ | —12.2 | 5.35(0.5366) | 8 |
|    |      |       | 1.80(0.6678) | 8 |
|    | $4s$ | —8.6 | 1.90 | present work |
|    | $4p$ | —4.8 | 1.90 | present work |

[a] Coefficients for the double $\zeta$ $3d$ orbitals in parenthesis

The E. H. calculations have been performed following our usual program.[5] Parameters where taken from the literature, sometimes with slight modification, and are collected in Table I. The repulsion effect of inner electrons in iron has been evaluated by means of the formula:

$$E(R_{Fe-N}) = 976.6 \exp(-4.230 R_{Fe-N})$$

where the energy $E$ is in eV and the iron-nitrogen distance is in Å.

### RESULTS AND DISCUSSION

The N₂ dissociation has been computed first. The minimum energy obtains at $R_{NN} = 0.085$ Å, significantly shorter than the experimental value 1.098.[4] Figure 2 shows that the energy of the highest occupied molecular orbital of N₂ lies in the energy range of the iron cluster orbitals so that from the interaction of the two systems no abnormal charge transfer effect is expected. It has been also found that the energy per atom is about the same for the seven calculated clusters.

The next calculation was the evaluation of the adsorption energy of atomic nitrogen according to the formula:

$$E_b = E_{cluster+N} - E_{cluster} - \frac{1}{2} E_{N_2}$$
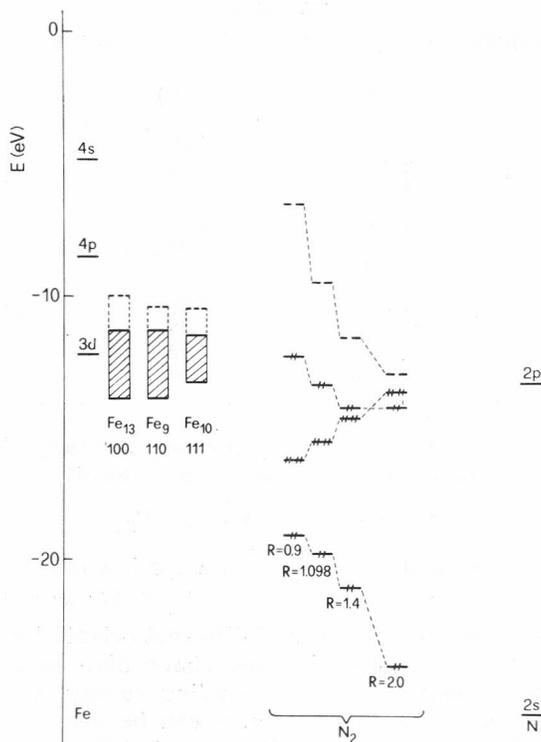


Figure 2. N₂ molecule orbitals energy levels at different N—N distances are shown with nitrogen atom orbital levels and energy bands for typical Feₓ clusters.
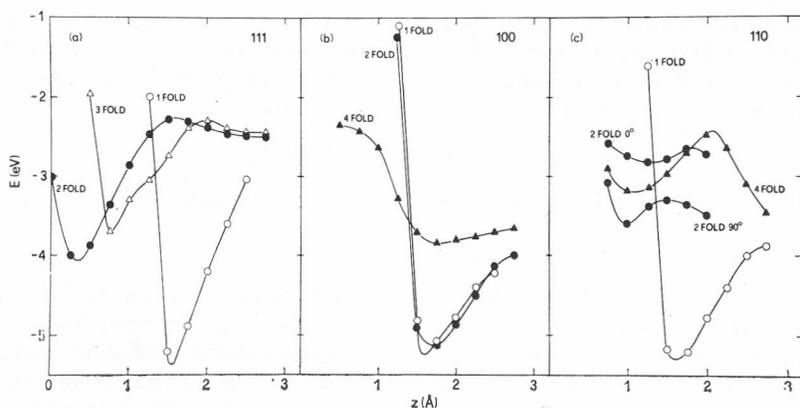
Figure 3. Atomic adsorption energy curves on plane 111 (a), 100 (b), and 110 (c).

The curves as a function of the distance $z$ between the N atom and the first metal atom layer are shown in Figure 3 (a), (b) and (c) for the (111)—(100) and (110) planes respectively. Table II collects the coordinates for the energy minima.

TABLE II

*Atomic Adsorption Energy on Different Sites as Defined in Figure 1*

| Plane | Site | $z/\text{Å}$ | $E_b/\text{eV}$ |
|-------|------|------|------|
| 100 | 1 fold | 1.60 | —2.63 |
|  | 2 fold | 1.70 | —2.57 |
|  | 4 fold | 1.75 | —1.91 |
| 111 | 1 fold | 1.50 | —2.69 |
|  | 2 fold | 0.35 | —2.01 |
|  | 3 fold | 0.75 | —1.84 |
| 110 | 1 fold | 1.55 | —2.64 |
|  | 2 fold (0°) | 1.25 | —1.41 |
|  | 2 fold (90°) | 1.00 | —1.80 |
|  | 4 fold | 1.00 | —1.59 |

A second set of calculations was performed to study the interaction of molecular nitrogen with the metal clusters. The adsorption energy is given by

$$E = E_{\text{cluster}+N_2} - E_{\text{cluster}} - E_{N_2}$$

The $R_{NN}$ distance was kept equal to the experimental value. The energy minima and the corresponding vertical distances are reported in Table III.

For each adsorption site a number of different orientations was considered. From the results it is clear that besides dissociative adsorption, molecular adsorption may be present, though the binding energy is about one half of that of the atomic case. The two processes can be defined as chemisorption and physisorption. We also considered the dissociation reaction of adsorbed $N_2$ to adsorbed 2 N; for each minimum geometry for the $N_2$ + cluster system, a path was followed in which $R_{NN}$ was progressively increased in order to

TABLE III

*Energies and Distances for Minima and Saddle Points of the $N_2$ + Cluster Systems. (The Symbol $\perp$ Means that $N_2$ is Perpendicular to the Surface)*

| Plane | Site | $\Theta$ deg. | Minimum $E_b$/eV | $z$/Å | $R_{NN}$/Å | Saddle point $z$/Å | $E_b$/eV | $\Delta E$/eV |
|---|---|---|---|---|---|---|---|---|
| 100 | 1 fold | $\perp$ | —2.01 | 1.66 | — | — | — | — |
|  | 1 fold | 0 | —0.93 | 1.83 | 1.31 | 1.65 | +0.07 | 1.00 |
|  | 1 fold | 45 | —1.10 | 1.80 | 1.47 | 1.61 | —0.42 | 0.67 |
|  | 4 fold | $\perp$ | —0.67 | 1.21 | — | — | — | — |
|  | 4 fold | 0 | —2.21 | 1.22 | 1.29 | 1.20 | —1.96 | 0.25 |
|  | 4 fold | 45 | —1.93 | 1.17 | 1.45 | 1.11 | —1.14 | 0.79 |
|  | 2 fold | 0 | —2.03 | 1.41 | 1.26 | 1.42 | —1.73 | 0.30 |
| 111 | 1 fold | $\perp$ | —2.63 | 1.62 | — | — | — | — |
|  | 1 fold | 0 | —1.39 | 1.75 | 1.40 | 1.58 | —0.62 | 0.77 |
|  | 1 fold | 30 | —1.39 | 1.75 | 1.40 | 1.58 | —0.66 | 0.73 |
|  | 3 fold | $\perp$ | —1.95 | 0.87 | — | — | — | — |
|  | 3 fold | 0 | —1.74 | 0.92 | 1.33 | 0.83 | —1.51 | 0.23 |
|  | 3 fold | 30 | —1.87 | 0.91 | 1.32 | 0.82 | —1.71 | 0.15 |
|  | 2 fold | 0 | —2.69 | 0.61 | 1.60 | 1.01 | —1.21 | 1.48 |
| 110 | 1 fold | $\perp$ | —2.02 | 1.63 | — | — | — | — |
|  | 1 fold | 0 | —1.19 | 1.73 | 1.44 | 1.59 | —0.74 | 0.45 |
|  | 1 fold | 90 | —1.04 | 1.69 | 1.42 | 1.55 | —0.66 | 0.38 |
|  | 4 fold | $\perp$ | —1.19 | 1.37 | — | — | — | — |
|  | 4 fold | 0 | —1.28 | 1.11 | 1.39 | 1.14 | —0.84 | 0.45 |
|  | 4 fold | 90 | —1.04 | 1.71 | 1.48 | 1.84 | —0.63 | 0.41 |
|  | 2 fold | 0 | —1.66 | 1.11 | 1.42 | 1.14 | —1.07 | 0.59 |
|  | 2 fold | 90 | —1.28 | 1.51 | 1.25 | 1.77 | —0.63 | 0.65 |

bring the two N atoms to the nearest sites corresponding to an energy minimum for atomic adsorption. Variation of the $z$ distance was allowed along the path. In this way sixteen potential energy surfaces were obtained, each representing $E = E(R_{NN}, z)$. Each surface contains one of the energy minima for the molecular adsorption and on each one a saddle point was found along the reaction path.

The difference in energy between the starting minimum and the saddle point was taken as the activation energy for the reaction along the path. The numerical results are shown in Table III. One example of this surface for each plane is shown in Figure 4. It must be mentioned that the surfaces are truncated at $R_{NN} = 1.098$ Å since it is not advisable to consider shorter N—N distances; in fact in the presence of the metal cluster the E. H. method calculates unrealistic equilibrium N—N distances, even shorter than the value obtained for the isolated $N_2$ molecule. In Figure 5 the energies along the least energy path, on the surfaces of Figure 4, are shown. From a thermodynamic point of view our results suggest that the most stable situation is atomic N adsorbed on the top of metal atoms of the 111 surface plane, the similar sites on the 100 and 110 planes being about at the same level of stability, and somewhat higher in energy than the previous one.

The kinetic approach represents a far more complicated problem. One should not be satisfied with the few sections of the energy hyperspace that we have considered. The complete potential hypersurface should be obtained and used to calculate trajectories at least of a semiclassical type.
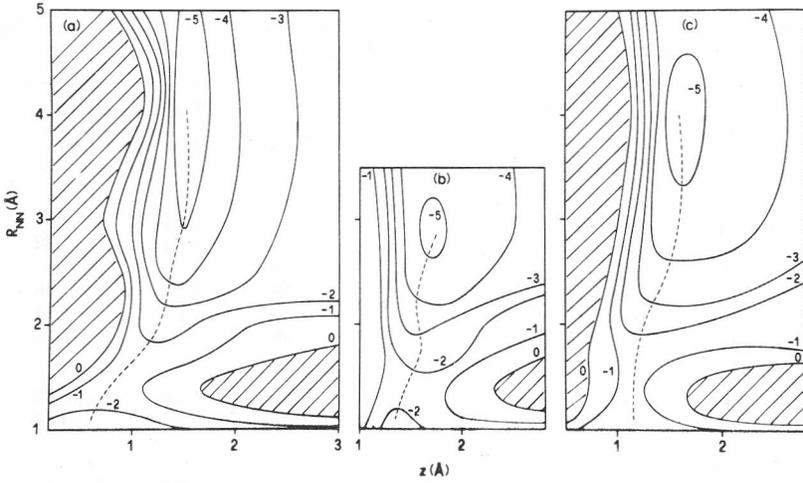
Figure 4. Potential energy surfaces $E = E(R_{NN}, z)$ for the 2-fold sites, $\Theta = 0$ orientation, on the planes: 111 (a), 100 (b), 110 (c). The numbers on each isoenergetic line give the energy value in eV.
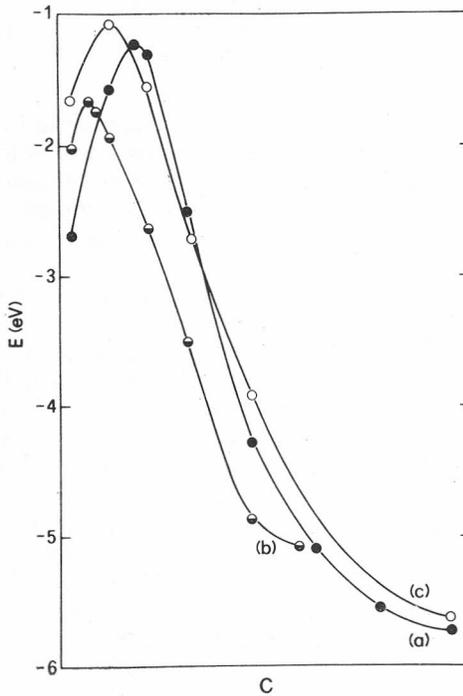


Figure 5. Energy (eV) along the dissociation coordinate C for the 2-fold sites, $\Theta = 0$ orientation, on the planes 111 (a), 100 (b), 110 (c).

Since different aiming points, different rotovibrational and different phases at the time of collision with the surface, different initial orientation of the molecule and of its plane of rotation and different velocities should be considered, the number of trajectories to be calculated in order to obtain a reliable value for the dissociation rate constant and the sticking coefficient is extremely high and so this dynamical approach is out of the range of our present calculation facilities.

We have to be satisfied with a rather primitive approach, that is the evaluation of the activation energy along the reaction paths that we have calculated.

This doesn't mean that we consider that only dissociation *via* molecular adsorption is obtained, but this is surely one of the favourable routes, and one for which calculations are possible. Of course within this drastic approximation only qualitative results can be expected: namely we can try a comparison of reactivity on different metal planes. From our results it appears that the reactivity order should be: 111 ($\Delta E = 0.15$ eV) $>$ 100 ($\Delta E = 0.25$ eV) $>$ 110 ($\Delta E = 0.38$ eV). Keeping in mind the initial assumption that $N_2$ dissociation is the rate determining step in ammonia synthesis on iron catalyst, it is gratifying that the same order of reactivity was obtained from ammonia synthesis kinetic experiments on iron single-crystal.[3]

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### SAŽETAK

**Teorijsko razmatranje utjecaja strukture površina na kemisorpciju dušika na monokristalu atoma željeza**

*Emanuele Ortoleva i Massimo Simonetta*

Energija Fe$_x$-grozdova ($x = 9, 10, 13, 15, 18$) koji služe kao modeli za simulaciju površinskih ploha 111, 100 i 110 monokristala željeza, ocijenjene su s pomoću proširene Hückelove metode (EH). Određen je slijedeći redoslijed reaktivnosti ploha za sintezu NH₃: 111 $>$ 100 $>$ 110. Rezultati su u skladu s eksperimentalnim podacima.