

Brief Reports

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Total-energy calculations for N₂ dissociation on Fe(111): Characterization of precursor and dissociative states

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The N₂ dissociation on Fe(111) is investigated by calculating total-energy surfaces within a linear combination of atomic orbitals type formalism. The two molecular precursor states, involving N₂ bound parallel and perpendicular to the surface, and the dissociative state are characterized by their geometry and total energy. The results of the calculation agree with recent experimental data.

The dissociation of molecular nitrogen on Fe is of importance both technologically—it is the rate-determining step^{1,2} in the Haber-Bosch process—and as a model catalytic reaction. Despite a large effort to obtain a microscopic understanding of this reaction,^{2,3} only recently two weakly chemisorbed states, γ -N₂ and α -N₂, were identified experimentally⁴ and shown to be the precursor states for the dissociation into the β -N state. This experimental investigation suggested that α -N₂, the direct precursor state of β -N, lies parallel to the surface and the relatively mobile γ -N₂, the precursor of α -N₂, is randomly oriented or possibly perpendicular to the surface. It is the aim of this paper to present the first microscopic total-energy calculation for the N₂ dissociation on Fe(111) and to characterize the precursor states by their geometry and energy. The total-energy surfaces will give further valuable information about the activation barrier between these states, the preferential dissociation path, and can be used as input for microscopic reaction rate calculations.

In order to obtain the total energy E_{tot} of the adsorption system for a large number of different geometries, the atom superposition and electron delocalization (ASED) technique⁵ has been used. Here, E_{tot} consists of an attractive molecular orbital energy, evaluated in an extended Hückel-

type formalism, and of a repulsive interatomic interaction due to Coulomb repulsion. Taking correct care of the symmetry in the rehybridization of atomic orbitals, and allowing for orbital energy shifts due to inter- and intra-atomic Coulomb interactions, this fast method seems appropriate especially for calculating total-energy surfaces E_{tot} (geometry) for molecular adsorption and dissociation on metal surfaces. In the past, ASED was successfully used to obtain the equilibrium geometry and force constants in adsorption systems⁶ and to calculate the effect of promoters and poisons in catalysis.⁷

The parameters used in the present calculation are given in Table I. For free N₂, using these parameters one obtains the equilibrium bond length $R_e = 1.15$ Å (experimental value 1.10 Å), the vibration frequency $\nu = 2352$ cm⁻¹ (expt. 2359 cm⁻¹) and the dissociation energy $D_e = 11.7$ eV (expt. 9.8 eV). The correct bond length and vibration frequency are especially important, since our main interest in adsorption studies is devoted to the local geometry and relative energy changes.

In order to make the calculation feasible, the adsorbate's 6 degrees of freedom are reduced to a two-dimensional parameter space for a physically plausible geometry. The atomic arrangement at the Fe(111) surface, which is

TABLE I. Atomic parameters used in the calculations: principal quantum number (n), ionization potential (IP) in eV, and orbital exponents (ζ). Double-zeta basis (with orbital coefficients C) has been used for the d levels of Fe.

Atom	s			p			d					
	n	IP	ζ	n	IP	ζ	n	IP	ζ_1	ζ_2	C_1	C_2
Fe ^a	4	-9.37	1.70	4	-5.83	1.40	3	-10.50	5.35	1.80	0.547	0.668
N ^b	2	-18.33	2.02	2	-12.53	2.02						

^aReference 8; paramagnetic Fe.

^b1.5 eV ionization potential increase and 0.1 increase in exponents applied to parameters from A. B. Anderson, R. Kötz, and E. Yeager, Chem. Phys. Lett. **82**, 130 (1981).

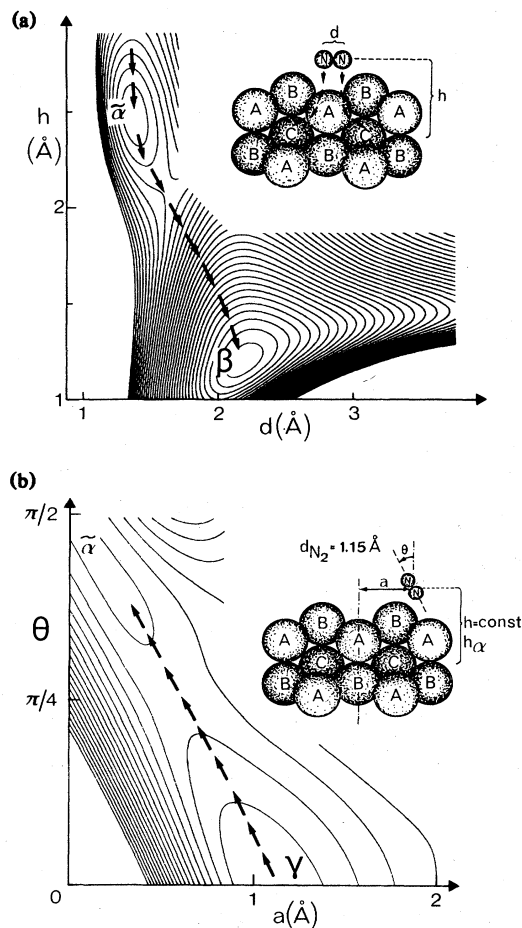


FIG. 1. Total-energy contour plot for the N_2 adsorption on Fe(111): (a) $E_{\text{tot}}(d, h)$ for the N_2 dissociation in the α geometry. d is the intramolecular distance and h the height with respect to third layer (C) atoms. (b) $E_{\text{tot}}(a, \theta)$ for the transition from γ - N_2 to α - N_2 in the γ geometry. a is the horizontal distance from the AB "edge" and θ is the tilting angle. The equidistant contours are separated by 0.2 eV. The preferential transition path is marked by arrows.

represented by a Fe_{12} cluster in the calculation, is given in the inset of Fig. 1. In the α geometry, which seems likely to describe the molecular dissociation, N_2 is assumed to lie parallel to the surface and to break apart at the "edge" formed by the neighboring top-layer (A) and second-layer (B) atoms, in order to get to the favorable hollow-site position on top of third-layer atoms (C). This geometry is also consistent with the observation of α - N_2 lying parallel to the surface.⁴

The results of this calculation are given as a contour plot in Fig. 1(a). The N_2 molecule, approaching the surface from the vacuum, first gets trapped in a weakly chemisorbed $\tilde{\alpha}$ state at a height $h_{\tilde{\alpha}} \approx 2.4$ Å and with an increased bond length $d_{\tilde{\alpha}} \approx 1.4$ Å. After surmounting a barrier $E_{\text{act}}^{\tilde{\alpha} \rightarrow \beta} \approx 0.4$ eV (expt.⁹ 0.3 eV) it dissociates into the β state by gaining 2.5 eV (expt.⁹ 2.1 eV) per N atom. Here, the N atoms are located at the hollow-site near the C atoms, at the height $h_{\beta} \approx 1.2$ Å and at a distance from these atoms which is nearly the sum of the Slater radii of Fe and N.

In order to better characterize the parallel N_2 states, we explored the total-energy surface near $\tilde{\alpha}$ perpendicular to the constraint plane. 0.3 Å off this plane, towards the "edge" B₂ atom, we found the α state at $h_{\alpha} \approx 2.1$ Å and $d_{\alpha} \approx 1.4$ Å, which was by ≤ 0.1 eV more stable than $\tilde{\alpha}$. This identification of the α state is further supported by the agreement of the vibration frequencies, contained in the curvature of the total-energy surface, with experimental data. With respect to the free molecule, the $^{15}N_2$ stretching frequency ν_{\parallel} in the α state dropped by half to $\nu_{\parallel} = 1381$ cm^{-1} (expt.⁴ 1490 cm^{-1}), mainly due to the occupation of the antibonding $1\tilde{\pi}_g$ orbital with 1.95 electrons. The $^{15}N_2$ -Fe frequency ν_{\perp} in the α state lies at $\nu_{\perp} = 367$ cm^{-1} (expt.⁴ 435 cm^{-1}). In addition to their similar geometry and energy, α and $\tilde{\alpha}$ resemble each other very much in their vibration frequencies and activation barriers. The minor differences between them do not affect our conclusions drawn from Fig. 1(a). In that calculation, we selected the α plane of constraint to discuss the N_2 dissociation, since it also contains the β state.

Next we investigate the transition from the weakly chemisorbed γ to the α state, our main interest being the molecular orientation. In the γ geometry, keeping the N_2 distance fixed at 1.15 Å and the height h at the value $h_{\tilde{\alpha}}$, the molecule is allowed to move horizontally between the AB edge and the C atoms (horizontal position defined by a) and to tilt by the angle θ [see also the inset in Fig. 1(b)]. The resulting total-energy surface is presented in Fig. 1(b). In a metastable state (denoted by γ) somewhat off the hollow-site center at $a \approx 1.1$ Å, N_2 is stable perpendicular to the surface. Moving the molecule towards the AB edge, it tilts off the perpendicular direction and, after surmounting a barrier, which in this model geometry amounts to $E_{\text{act}}^{\gamma \rightarrow \tilde{\alpha}} = 0.4$ eV (expt.⁹ 0.2 eV), it turns parallel to the surface in the $\tilde{\alpha}$ state.

In the different γ' geometry, keeping the N_2 molecule on top of the AB edge ($a = 0$) with a fixed bond length $d = 1.15$ Å and varying the height h and the tilting angle θ , one also obtains a metastable γ state bound perpendicular to the surface at a large height $h \approx 3.4$ Å and a parallel-lying $\tilde{\alpha}$ state at $h \approx h_{\alpha}$. The activation barrier for the transition in this geometry seems to be of the order of 1 eV. Hence, the main conclusions about the orientation of γ - N_2 and α - N_2 agree with experiment.

Finally, some remarks concerning the reliability of the presented results. In this calculation, it has been assumed that the adsorbate and substrate level shifts (with respect to free atoms) are constant when the geometry of the adsorption system is changed. This assumption can be justified if the distances between the adsorbate and the substrate atoms do not change. This applies along the preferential dissociation paths in the γ geometry and in the α geometry only between $h_{\tilde{\alpha}}$ and h_{β} and hence does not affect the resulting activation barriers and energy differences. On the other hand, this assumption does not hold in the α geometry for $h \geq h_{\tilde{\alpha}}$ and in the γ' geometry where quantitative predictions are less reliable. Our next remark concerns the restriction of the degrees of freedom imposed to the system in the calculation. Clearly, during the transition from the γ to $\tilde{\alpha}$ state, at each value of a , the molecular bond length and the vertical position of its center of gravity are expected to relax. These relaxations, not taken into account in the γ geometry, are expected to result in a decrease of the activa-

tion barrier. As already mentioned above, the ASED method has been used to calculate relative energy changes rather than the adsorption energy E_{ads} of the molecule, mainly due to uncertainties in the orbital energy shift upon desorption. In view of this uncertainty, using a rough approximation for these orbital shifts,¹⁰ the estimated values of $E_{\text{ads}}(\gamma) \approx 1.3$ eV (relaxed geometry) and $E_{\text{ads}}(\alpha) \approx 1.1$ eV compare well with the experimental values⁹ 0.2 and 0.3 eV in the γ and α states, respectively. Furthermore, note that we performed our calculation for paramagnetic Fe. Presently it remains unclear which role magnetic effects play on adsorption.

It would be interesting to extend and to compare the present calculations of the microscopic dissociation mechanism to other systems.¹¹ While generally on transition metals both perpendicular and parallel adsorption states are expected, it seems likely that on *sp* metals (Ag, Au, etc.) the parallel state is more pronounced and a perpendicular state eventually does not exist. A very similar adsorption behavior is also expected on close-packed as compared to open surfaces. On the other hand, polar molecules are ex-

pected to prefer perpendicular adsorption on transition metals.

Our present knowledge of the microscopic N_2 dissociation mechanism on Fe(111) can be finally summarized as follows. A free N_2 molecule first gets trapped into a highly mobile γ state (perpendicular N_2) in order to get rid of its excessive energy. At appropriate sites (such as the hollow *C* sites), after surmounting a barrier $E_{\text{act}}^{\gamma \rightarrow \alpha} \approx 0.4$ eV, N_2 tilts over to a parallel-bound α state at the *AB* edge. From this state, after crossing the activation barrier $E_{\text{act}}^{\alpha \rightarrow \beta} \approx 0.4$ eV, N_2 dissociates into the neighboring hollow sites on top of the *C* atoms by releasing ≈ 2.5 eV per N atom. Clearly, many other ways will lead to dissociation, but they are energetically less favorable.

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²For a review, see M. Grunze, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1982), Vol. 4, p. 143ff.

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⁹M. Grunze, M. Golze, J. Fuhler, M. Neumann, and E. Schwarz, *Proceedings of the 8th International Congress on Catalysis, Berlin* (Verlag Chemie, Weinheim, 1984), p. IV-133ff.

¹⁰The rigid upward shift by 1.5 eV of the N orbitals upon adsorption has been reset in the desorbed molecule when calculating the adsorption energy. Note, similar shifts have been assumed previously in order to mimic self-consistency (see, e.g., Ref. 8) and compare well with observed core-level shifts.

¹¹D. Tománek and K. H. Bennemann (unpublished).