

SURFACE SCIENCE LETTERS

A QUANTUM MECHANICAL MECHANISM FOR THE DISSOCIATIVE CHEMISORPTION OF N₂ ON METAL SURFACES

M. ASSCHER, O.M. BECKER, G. HAASE and R. KOSLOFF

Department of Physical Chemistry and The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

Received 21 July 1988; accepted for publication 6 September 1988

The time dependent Schrödinger equation was numerically solved for the transition dynamics from the N₂-metal to the N-metal to the N-metal potential energy surfaces. The resulting rapid increase of the dissociation probability (S_0) with incident kinetic energy, its saturation at high energies and vibrational enhancement are in good agreement with recent experiments. A novel explanation for the small value of S_0 is based on the high energy value of the crossing region between the two potentials, predicting that the dissociation occurs via a tunneling mechanism. Recombinative desorption experiments of ¹⁴N₂ and ¹⁵N₂ from Re(0001) are in excellent agreement with the tunneling model.

Dissociative chemisorption on surfaces is amongst the most important primary steps in heterogeneous catalysis [1]. Perhaps the best studied example of such a process is that of nitrogen molecules on metal surfaces. Nitrogen dissociation is believed to be the rate limiting step of the high pressure ammonia synthesis from N₂ and H₂ [2–5]. Extensive studies have focused in recent years on the characterization of the kinetics of nitrogen interaction with clean and potassium promoted Fe(111) surfaces, which is the most active surface as an ammonia catalyst [6–11]. These studies concentrated on the identification and characterization of an α -N₂ molecular state, which is thought to be the direct precursor to dissociation on Fe(111) [8–11]. No such state was found on other iron single crystal surfaces, in spite of the similarity in the initial dissociative sticking probability (S_0) (Fe(111) is 60 times more active than Fe(110), but on all surfaces $S_0 \approx 10^{-6}$ – 10^{-7}) [4].

Other catalysts were recently studied, such as rhenium [12–15] for which a surprising similarity to iron was reported: the same apparent activation energy of 81.5 kJ/mol and the overall rate for the ammonia production [5,13].

In both systems, a central and open question is the apparent contradiction between the observed low activation energy barrier for the rate limiting step of N₂ dissociation (typically a few kJ/mol with a somewhat negative barrier on Fe(111)) and the overall very low ($\sim 10^{-4}$ – 10^{-7}) probability for dissociative

chemisorption on both metals. Moreover, a dramatic enhancement of the dissociation probability of N_2 on Fe(111) [16] due to increased incident kinetic energy together with the apparent activation energy of the ammonia synthesis, imply the existence of a far larger energy barrier.

In order to elucidate the governing physical phenomena this work presents a model quantum mechanical calculation of the dissociative chemisorption of N_2 . In these calculations it is stated that the reaction takes place on at least two electronically distinct potential energy surfaces (PES) which are the weakly bound molecular nitrogen-metal PES and the strongly bound atomic nitrogen-metal PES.

Most of the previous calculations of the dissociation of molecules on metal surfaces utilized classical mechanics for example H_2 [17], N_2 [18] and I_2 [19]. Quantum mechanical treatments for the dissociation of molecules have been limited to H_2 , on a single PES [20,21].

The model calculations presented in this Letter are based on an exact quantum mechanical evaluation of the transition probability of an incident wavepacket, propagating on the initial molecular potential energy surface (PES) (an admolecule PES - V_1) to a final dissociative state (an adatom PES - V_2). Although it is possible that more than two PES's are involved in the dissociative chemisorption event of a nitrogen molecule, as was recently suggested for the N_2 -Fe(111) system [11], evidence is provided that the actual quantum mechanical dynamics of this system can be correctly described by two effective potential energy surfaces. The extremely low dissociation probability (S_0) of N_2 (at thermal energies) on both iron and rhenium surfaces (10^{-7} - 10^{-4}), make classical trajectory calculations highly impractical. For such rare events, quantum mechanical treatments become more efficient in addition to being physically more correct.

In order to focus on the central dynamical features of the dissociation event and to reduce computation time the calculation was limited to two degrees of freedom: the N_2 -surface distance and the N-N distance.

The initial and final PES's (V_1 and V_2) were empirically constructed to mimic the interaction between N_2 and Re(0001) surfaces following TPD [14] and HREELS [22] data. Being very similar to the N_2 -iron system [23], we regard the chosen potentials as representing qualitatively both metals. V_1 and V_2 are constructed from Morse potentials for the vibrational degrees of freedom and a modified Morse function for the N_2 -surface coordinate. For the dissociation channel a repulsive exponential term was used. The potential parameters were fitted to give the known asymptotic vibrational frequencies and dissociation energies of the N_2 motion, the N_2 -metal motion and the N-metal motion. The values of the equilibrium vibrational distances on the surface were adjusted to give the barrier height of 73 kJ/mol. Details of the potentials will be published in a subsequent paper [24]. One of the most important features of the potentials is the intersection between V_1 and V_2 (the

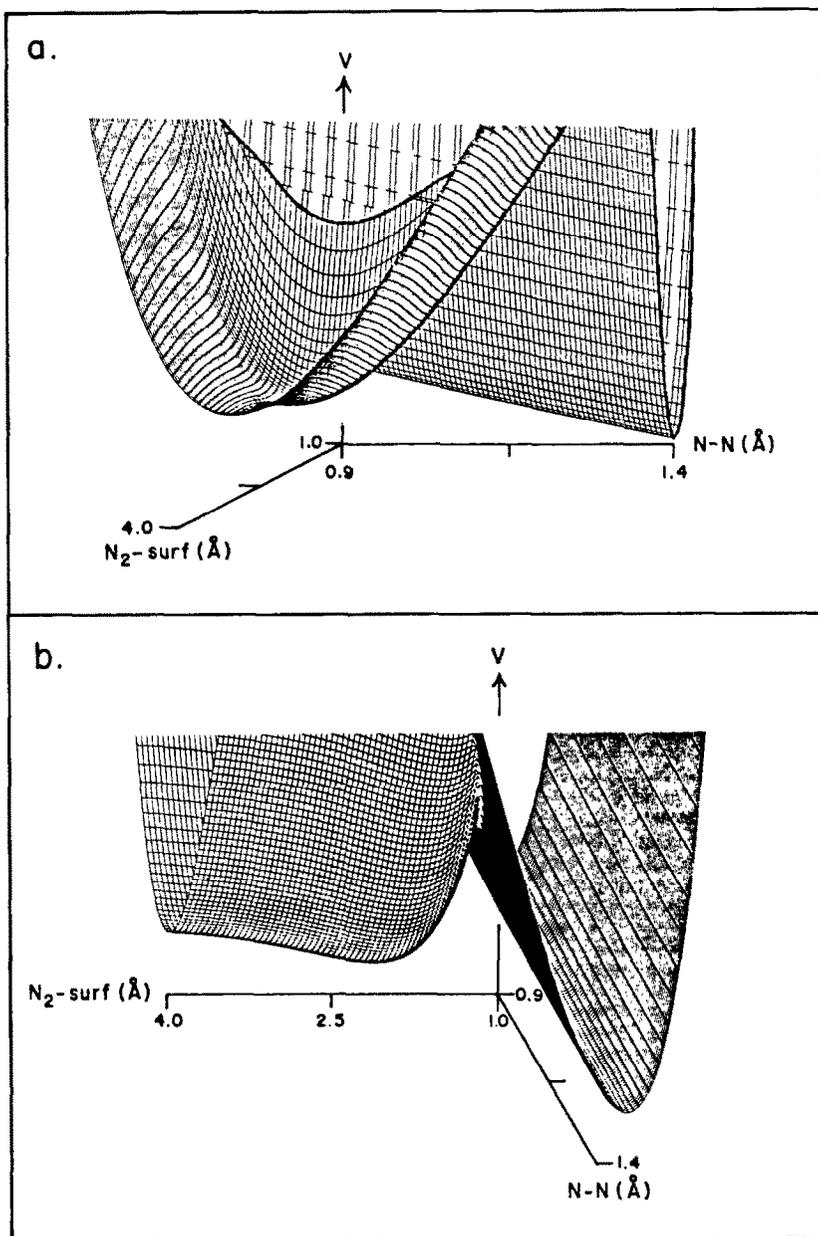


Fig. 1. (a) Perspective view of the N_2 -metal (V_1) and the N-metal (V_2) potential energy surfaces. (b) This view demonstrates the origin of the high barrier between the two potentials, due to crossing at the repulsive walls.

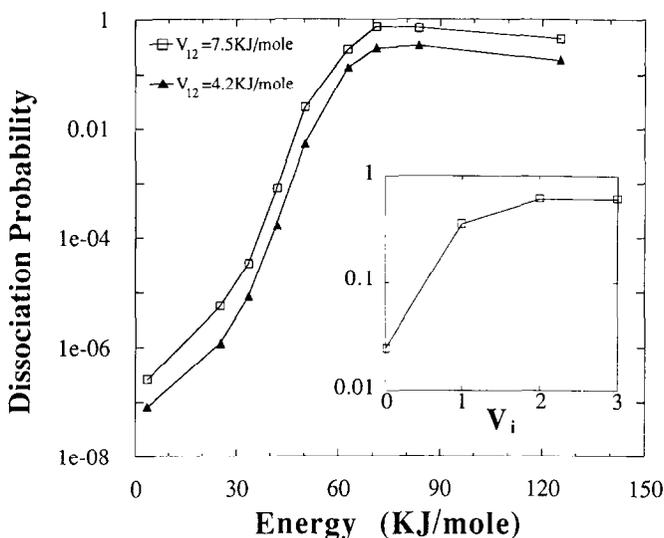


Fig. 2. Dissociation probability of N_2 as a function of incident kinetic energy (normal to the surface); the insert shows the effect of vibrational excitation on the dissociation at a kinetic energy of 50.2 kJ/mol.

seam). The shape and energy range of this seam are crucial in determining the dissociation probability. Two parameters influence the geometry of the seam: (a) the relative distance from the surface (z -direction in fig. 1) of the minima of the two potentials, (b) the steepness of the repulsive wall of the molecular surface and the steepness of N-surface vibration wall (see fig. 1).

As might be expected, the dissociation probability is extremely sensitive to the coupling term V_{12} between V_1 and V_2 . This parameter was chosen to have the form of an exponentially decreasing function in both the N-N and the N-surface distances. In order to demonstrate the sensitivity of S_0 to V_{12} , two different interaction parameters were used, leading to $V_{12} = 4.2$ kJ/mol and $V_{12} = 7.5$ kJ/mol, at the minimum of the seam, as shown in fig. 2.

In fig. 1a the perspective view of the two PES's is displayed. Note the parabolic-like shape of the seam, which is 73 kJ/mol above the N_2 gas phase energy. Fig. 1b clarifies the origin of that high barrier, due to the difference in the distance of the minimum of the two potentials from the metal surface. Note also that the seam lies slightly on the side of the repulsive wall of V_1 . This affects the importance of incident vibrational excitation on the dissociation event.

Once the potential energy surfaces have been constructed, the detailed quantum dynamics is calculated. The route chosen is to solve the time dependent Schrödinger equation. This method is an initial value problem, therefore it is geared to calculate the relevant information: the dissociation

probability as a function of the initial state. For this reason the initial state was chosen to be a product of the vibrational wavefunction for the gas phase N₂ state (calculated by the relaxation method [25]) and a Gaussian wave function for the translational degree of freedom. The initial average momentum was chosen to match the desired kinetic energy. The width of the Gaussian was chosen to mimic a velocity spread in a typical experimental supersonic beam. The numerical method used to solve the time dependent Schrödinger equation was a two-surface modification of the Fourier–Chebyshev method. The details of the method have been described previously [26]. The convergence of the calculation has been tested by increasing the grid density and was found accurate enough to give dissociation probabilities of less than 10⁻¹⁰.

The results of the calculations on the effect of incident kinetic energy of N₂ on the dissociation probability are shown in fig. 2. The exponential increase of the dissociation probability with incident kinetic energy almost exactly reproduces the experimental results of Rettner et al. [16] for the N₂–Fe(111) system. The saturation effect observed at incident energies above the barrier level, was also reported experimentally [16]. It seems that the value of S₀ at which the curve in fig. 2 levels off is rather sensitive to the coupling term V₁₂. These results provide a quantum mechanical insight for understanding the origin of the experimentally observed saturation of S₀. It appears as if the V₁₂ parameter, which determines the maximum dissociation probability is crucial for explaining structure sensitivity or the ability of different single crystal faces to dissociate N₂ at different rates.

Finite probability to overcome a barrier of 73 kJ/mol at incident energies lower than that may be explained quantum mechanically by a tunneling mechanism on an adiabatic surface. The somewhat faster than exponential increase of the dissociation probability with incident N₂ kinetic energy (fig. 2) clearly reflects the effect of both the height and the width of the barrier between V₁ and V₂, on the transition probability through the barrier. In order to further demonstrate the tunneling mechanism, a set of calculations was performed with mass 30 (¹⁵N₂) rather than 28 (¹⁴N₂) at an incident energy of 25 kJ/mol. The dissociation probability is 0.64 of the ¹⁴N₂ value. An order of magnitude estimation of the tunneling probability can be obtained by using a one-dimensional semiclassical approximation:

$$p \approx \exp\left(-\frac{(2m)^{1/2}}{\hbar} \int_0^L (V-E)^{1/2} dx\right),$$

where *m* and *E* are the particle's mass and incident energy, respectively, and *L* is the barrier width. For a parabolic potential the ratio between the dissociation probability of the two isotopes is 0.68 for S₀ ≈ 10⁻⁵. In an attempt to obtain a preliminary experimental verification of the tunneling mode, we performed thermal programmed desorption experiments (TPD) with

nitrogen molecules at mass 28 ($^{14}N_2$) and mass 30 ($^{15}N_2$). Details of the experimental part are given elsewhere [24]. It was found that $S_0(^{15}N_2)/S_0(^{14}N_2) = 0.75 \pm 0.1$ with $S_0(^{14}N_2) \approx 10^{-5}$ on Re(0001) at 293 K, in excellent agreement with the calculated mass effect on the tunneling rate. The tunneling explanation for the low dissociation probability should be compared with a classical explanation in which the Boltzmann tail of the thermal distribution is above the dissociation barrier, which would lead to $S_0 \approx 10^{-12}$ for a barrier of 73 kJ/mol.

The tunneling mechanism for dissociative chemisorption of molecules was previously suggested for hydrogen containing molecules like CH_4 by Winters [27] and later by Rettner et al. [28] and Ceyer and coworkers [29]. A specific calculation of a tunneling process was given by Holloway et al. [21], who modeled the dissociation of H_2 on metal surfaces. Their potentials were taken from an ab initio total energy calculation for the H_2/Cu system. In this paper these authors suggested that the similar behavior found for H_2 , CH_4 and N_2 implies that the tunneling mechanism may apply also for the $N_2/Fe(111)$ system. No further details, however, were given to substantiate this statement.

Finally, the vibrational energy of the incident molecules was changed in order to check its effect on S_0 (see fig. 2). An order of magnitude enhancement is observed by changing the incident vibrational level (V_i) from $V_i = 0$ to $V_i = 1$, with additional moderate increase for $V_i = 2$ and then no further enhancement of S_0 for $V_i = 3$. The overall increase in S_0 due to the vibrational energy of the incident molecules is in agreement with a recent experiment done by Rettner et al. [30]. They estimate on the average a lower effect for the vibrationally excited molecules, when compared with translational energy of equal magnitude. When inspecting the effect of $V_i = 1$ (15% population at 2000 K, the experimental conditions) one observes a quantitative agreement with the results presented at fig. 2.

We should, however, note that the small differences between the calculations and the experimental results may arise from the crystal temperature, which was not taken into account in the present work.

The results shown in the insert of fig. 2 for the effect of vibrational excitation on the dissociation of N_2 are dependent upon the position and shape of the seam (see fig. 1). In a different setup of V_1 relative to V_2 , in which the seam is further on the side of the repulsive molecular PES, an enhanced effect of the vibrational excitation was found. The sensitivity of S_0 to vibrational excitation can serve, therefore, as a convenient experimental tool for estimation of important PES parameters such as the position and shape of the seam, as was suggested by Holloway et al. [21]. A supporting evidence has been reported for the reverse process of recombinative desorption of N_2 . The experiment was performed on a clean and sulfur-covered iron foil, where different vibrational excitation was detected for the two surfaces [31]. These results were discussed in terms of such a change in the position of the seam.

In conclusion, we have demonstrated that exact quantum mechanical calculations predict correctly the effect of incident kinetic energy of the nitrogen molecules on its dissociation probability. These calculations were performed by computing the transition probability from the molecular-surface PES (V_1) to the atomic-surface PES (V_2), employing the time dependent Schrödinger equation. We found that the dissociation of nitrogen on metal surfaces, such as rhenium and iron, can be described as a tunneling phenomenon. The results of preliminary TPD experiments with $^{15}N_2$ and $^{14}N_2$ support the tunneling model.

Relatively large effects of vibrational excitation of the incident molecules on the dissociation probability are found.

Fruitful discussions with C. Cerjan, B. Gerber, and R.D. Levine are gratefully acknowledged. This work was partially supported by the United States Israel Binational Foundation and the Israel National Academy of Science and Humanities. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, mbH, München, Fed. Rep. of Germany.

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