

# Tunneling mechanism for the dissociative chemisorption of $N_2$ on metal surfaces

M Asscher, G Haase and R Kosloff, *Department of Physical Chemistry and The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel*

*A quantum mechanical tunneling mechanism is found to describe accurately recent experimental study on the dissociative chemisorption dynamics of nitrogen molecules on metal surfaces. A numerical treatment of the time-dependent Schrödinger equation was employed to evaluate the transition probability ( $S$ ) from  $N_2$ -metal to N-metal potential energy surfaces (PES) for two degrees of freedom on a flat and rigid surface. The rapid increase of  $S$  with incident kinetic energy, its saturation at energies above the barrier for dissociation and vibrational excitation effects were all in good agreement with the experimental results. The calculated results were found to be very sensitive to the potential topology at the crossing area (seam) between the two PES. This extreme sensitivity may serve as a calibration method for the potential shape, by using experimental data for the relative importance of vibration to translation in promoting the dissociation. Large isotope effects are predicted and confirmed by temperature programmed recombinative desorption experiments of  $^{14}N_2$  and  $^{15}N_2$  from Re(0001).*

## 1. Introduction

The interaction of nitrogen molecules with metal surfaces, and in particular its dissociation has been the subject of intensive research for more than 80 years. This is mostly due to the industrially important heterogeneously catalysed ammonia synthesis from nitrogen and hydrogen over iron catalysts as found by Haber and van Oordt 1904<sup>1</sup>. In this process the nitrogen dissociative chemisorption is the rate limiting step.

In spite of the research effort made, there are still a few open questions as to the detailed dynamics which lead to  $N_2$  dissociation on iron<sup>2,3</sup> and other ammonia synthesis catalysts such as rhenium<sup>4,5</sup>. An apparent contradiction between crystal temperature effects on the dissociative chemisorption probability ( $S_0$ ) measured for  $N_2$  on iron<sup>2,3</sup> and rhenium<sup>4</sup> and the extremely low value of  $S_0$  measured on both metal surfaces, is the major motivation for this paper. The crystal temperature effects mentioned above, predict a relatively low barrier for the dissociation of  $N_2$ , only 12–21 kJ mol<sup>-1</sup>. These cannot explain the dissociation probability of  $10^{-7}$  and  $10^{-5}$  measured on iron and rhenium, respectively. A recent molecular beam-surface scattering experiment<sup>6,7</sup> in which  $N_2$  molecules were accelerated to a Fe(111) surface suggest a far higher barrier to dissociation, of the order of  $\sim 100$  kJ mol<sup>-1</sup>.

These facts have led us to suggest a quantum mechanical approach for the dissociation dynamics of  $N_2$ <sup>8,9</sup>. A large barrier for dissociation was assumed, as the molecular beam experiments on Fe(111) implied<sup>6</sup>, and full two-dimensional quantum mechanical calculations were performed to simulate the  $N_2$  dissociation dynamics. As a result of these calculations, temperature programmed desorption (TPD) experiments of  $^{14}N_2$  and  $^{15}N_2$  were performed to examine the large isotope effect predicted by the calculations.

We concluded that the dissociation dynamics of  $N_2$  on metal surfaces such as iron and rhenium is consistent with a quantum mechanical tunneling of the gas phase nitrogen molecules through an energy barrier to the products channel of nitrogen

adatoms, chemisorbed on the surface. Quantum mechanical treatments were previously suggested as a possible explanation for the dissociation of hydrogen containing molecules<sup>10</sup>. Tunneling was mentioned before also for methane and nitrogen dissociation, although not calculated specifically for these molecules<sup>11</sup>.

## 2. Results and discussion

**2.1. Method of calculation.** The most sensitive part of a calculation of this kind is the construction of a potential energy surface (PES) on which the dynamics take place. Since *ab initio* cluster calculations are not available to describe the  $N_2$ -iron or  $N_2$ -rhenium systems, we have adopted an empirical approach based on the data of TPD and high resolution electron energy loss experiments<sup>9</sup>. These experiments provide information on the well depth and the stretch frequency as an input for both  $N_2$ -metal ( $V_1$ ) and the N-metal ( $V_2$ ) potentials. The potentials have a Morse-like form. The most important unknowns in these empirical potentials are the equilibrium distances along the  $z$  direction which are the distances of the  $N_2$  molecule in its well, and the atomic nitrogen in its well. Based on a recent EXAFS study, the N-metal equilibrium distance was fixed at 1.8 Å while the  $N_2$ -metal distance was an adjustable parameter. This was used to construct a barrier to dissociation of our choice: at a bottom-of-the-well ( $N_2$ -metal) distance of 2.8 Å away from the surface, a barrier of 73 kJ mol<sup>-1</sup> is found. This value represents the height in this part of the two potentials  $V_1$  and  $V_2$  which intersect to form a parabolic seam, the minimum of which is 73 kJ mol<sup>-1</sup> above the gas phase  $N_2$  energy, at zero incident kinetic energy. The barrier to dissociation therefore originates from the fact that the two Morse-like potentials intersect on the steep repulsive part of the  $V_1$  potential. Thus, the two coordinates of our calculations are the  $N_2$  center-of-mass-metal distance ( $z$ -coordinate) and the N-N distance ( $r$ -coordinate). Once both PES's are constructed, the quantum dynamics of the

problem should then be treated. This is done by numerically solving the time-dependent Schrödinger equation following the representation of the wave function on a spatial grid distributed on the chosen set of coordinates near the collision region of the potential<sup>9,12</sup>. The initial state of the problem represents a nitrogen molecule approaching the surface from the gas phase. As a result, the wave function is given by a product of a vibrational wave function in the *r*-direction and a translational wave function in the *z*-direction. The wavepacket is located on the molecular PES.

Once the PES and the initial states are defined, the wave function is propagated in time to obtain the detailed dynamics. The method of propagation is a modification of the Fourier Chebychev method<sup>12</sup>. The Hamiltonian operator has a (2 × 2) matrix form:

$$\hat{H} = \begin{bmatrix} \hat{H}_1 & \hat{V}_{12} \\ \hat{V}_{21} & \hat{H}_2 \end{bmatrix}$$

where the coupling potential is  $\hat{V}_{12}$ . The details of the key steps of the calculation of the Hamiltonian operator and the exact propagation method are given elsewhere<sup>9</sup>.

**2.2. Results.** The dissociation probability ( $S_0$ ) of N<sub>2</sub> was defined as the ratio of the squared amplitude of the wave function transmitted, to the  $V_2$  (chemisorption) potential by that remaining on  $V_1$ , the molecular state.  $S_0$  was calculated as a function of incident kinetic energy for a vibrational ground state molecule, with an incident translational energy spread of 0.042 kJ mol<sup>-1</sup>. It was found that  $S_0$  increases exponentially from  $\sim 10^{-7}$  at incident translational energy of 4 kJ mol<sup>-1</sup> to near unity at incident energy of 84 kJ mol<sup>-1</sup>, the barrier for dissociation being 73 kJ mol<sup>-1</sup>. This was obtained for a coupling potential  $V_{12} = 4.2$  kJ mol<sup>-1</sup>. These results are qualitatively similar to those reported experimentally for the N<sub>2</sub>-Fe(111) system<sup>6</sup>. The major differences between the calculated and the experimentally measured values of  $S_0$  are in the somewhat slower rise of the experimental  $S_0$  with incident translational energy and its lower saturation value at incident energies higher than the barrier height.

No attempt was made to best-fit the experimental data of Rettner and Stein<sup>6</sup> by making the necessary changes in the PES, since the potential was constructed for N<sub>2</sub>-Re(0001) (although these two systems are remarkably similar). Nevertheless, we believe that by reducing  $V_{12}$  from 4.2 to 0.5 kJ mol<sup>-1</sup> and considering the fact that the calculation was performed for a rigid surface, the calculations reproduce the main features of the experimental results quite nicely.

Next, the effect of incident vibrational excitation was studied. It was found that excited vibrational states are effective in enhancing the dissociation, but not as much as the effect of an equivalent amount of energy in translation. Very similar qualitative conclusions were reported by Stein and Rettner<sup>7</sup> for the N<sub>2</sub>-Fe(111) system.

Since the results described above imply the possibility that a quantum mechanical tunneling mechanism is involved in the dissociative chemisorption process, an isotope effect was calculated. By employing the full quantum mechanical machinery and by approximating the tunneling rate with a one-dimensional semi-classical expression, the ratio  $S_0(^{15}\text{N}_2)$  to  $S_0(^{14}\text{N}_2)$  was calculated. In both cases it was found that the ratio is incident energy-dependent. For a barrier for dissociation which leads to

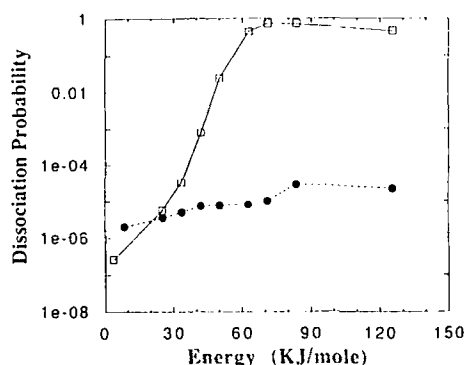
$S_0(^{14}\text{N}_2)$  of  $\sim 10^{-5}$  for a room temperature Boltzmann distribution of incident molecules, the isotope effect was calculated to be 0.75. This number was then checked experimentally by employing a temperature programmed recombinative desorption (TPRD) experiment for  $^{14}\text{N}_2$  and  $^{15}\text{N}_2$  from Re(0001), where  $S_0(^{14}\text{N}_2)$  was previously reported to be  $\sim 10^{-5}$ .<sup>4</sup> It was found that under carefully controlled conditions, the  $^{15}\text{N}_2$  is slower to dissociate at all exposures, with a ratio  $S(^{15}\text{N}_2)$  to  $S(^{14}\text{N}_2)$  extrapolated to a zero coverage of  $0.72 \pm 0.1$ . This is in excellent agreement with the calculated value and therefore strongly supports the tunneling model.

A brief inspection of the effect of the potential topology, and in particular the effect the position of the seam has on the overall effects studied before, has been performed as well. The position of the seam has been arbitrarily changed by altering the equilibrium distances of  $V_1$  and  $V_2$ , such that the barrier at the seam is unchanged (73 kJ mol<sup>-1</sup>) but the position of the seam has been shifted strongly to the side of the molecular N<sub>2</sub>-metal potential, perpendicular to the N-N vibration. The potential was transformed into an exit channel barrier type. The results of the calculations over this potential show a dramatic decrease in the effect of the incident kinetic energy on the dissociation. Even for incident kinetic energies above the barrier,  $S_0$  remains very low ( $10^{-5}$ ). However, the vibrational excitation becomes extremely important in enhancing the dissociation. Changing the incident vibrational state from  $v = 0$  to  $v = 2$  at the same incident kinetic energy, increased  $S_0$  by more than 4 orders of magnitude, from  $\sim 10^{-5}$  to 0.3 for incident kinetic energy of 50 kJ mol<sup>-1</sup>. In Figure 1 the effect of the kinetic energy on  $S_0$  in the regular, and the shifted, barrier potentials is demonstrated, and the vibrational excitation effect on  $S_0$  for the two PES is shown in Figure 2. In an attempt to study further the details of the potential shape near the seam, the form of the molecular-metal potential has been changed into an exponential with long-range dispersive forces:

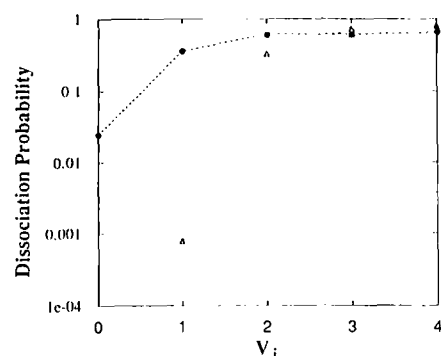
$$V^1(z) = e^{-\alpha z} - \left(1 - \frac{\Gamma(z)C_3}{z^3}\right).$$

The parameters for the choice of  $C_3$  were taken from ref 13 and  $\Gamma(z)$  is the incomplete gamma function.

This modification has made the barrier for dissociation somewhat narrower than with the previous Morse-type potential. As a result the tunneling rate has increased by about a factor of two,



**Figure 1.** The effect of incident kinetic energy on the dissociation probability ( $S_0$ ) is shown for the entrance-channel-barrier (open squares) and exit-channel-barrier (filled circles) potential energy surfaces. The coupling term  $V_{12} = 7.5$  kJ mol<sup>-1</sup> in both cases.



**Figure 2.** The effect of incident vibrational energy on  $S_0$ . The open triangles and filled circles are the exit-channel-barrier and entrance-channel-barrier potentials, respectively. In both cases the incident kinetic energy is  $50 \text{ kJ mol}^{-1}$  and  $V_{12} = 7.5 \text{ kJ mol}^{-1}$  (for  $V = 0$ ,  $S_0 = 8 \times 10^{-6}$ ).

even though exact comparison is difficult since the seam position has slightly shifted due to this modification.

Finally, very preliminary molecular beam experiments where N<sub>2</sub> molecules are accelerated to a Re(0001) single crystal surface under uhv conditions are under way. The detection of the dissociation rate was done by TPD as a function of crystal temperature and incident N<sub>2</sub> kinetic energy. For the limited range of normal component of the incident energy of 17–30 kJ mol<sup>-1</sup> it is found that kinetic energy increases the dissociation probability by an order of magnitude, where the calculated

values for an entrance-channel-barrier type of potential, predict an increase of 3 orders of magnitude. These results may imply that on Re(0001), an exit channel potential is more appropriate to describe the system. This will be more carefully checked in the near future by measuring the effect of vibrational excitation on  $S_0$ .

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