

Dissociative Chemisorption of N₂ on Ru(001) Enhanced by Vibrational and Kinetic Energy: Molecular Beam Experiments and Quantum Mechanical Calculations

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The dissociation probability of N₂ on Ru(001) increases from 5×10^{-7} at a kinetic energy of 0.15 eV to 10^{-2} at 4.0 eV. Vibrational excitation of the impinging nitrogen molecules enhances the dissociation more than the equivalent energy in translation. Its relative importance increases as the incident kinetic energy grows. The dissociation was found to be surface temperature independent at all incident kinetic energies, in agreement with theoretical predictions based on quantum mechanical nonadiabatic calculations. These simulations reproduce accurately the kinetic energy dependence of S_0 over the entire energy range, suggesting that N₂ tunnels from the molecular to the adsorbed atomic state through an effective barrier of 2.2 eV.

I. Introduction

Dissociative chemisorption of molecular nitrogen on metal surfaces is of fundamental as well as practical importance. In ammonia synthesis nitrogen dissociation is the rate-limiting step over industrial iron-based catalysts. Therefore it has been investigated more than any other heterogeneous catalytic reaction.^{1,2} New insight into the dissociation dynamics has been obtained due to molecular beam experiments of the dissociation of N₂ on W(110),³ Fe(111)^{4,5} and Re(001).⁶ These studies have shown dramatic enhancement of the dissociative sticking probability (S_0) upon acceleration of the incoming molecules. Quantum mechanical analysis of the results has suggested a *tunneling* mechanism of the molecular nitrogen through a significant potential energy barrier.^{7–11} The possibility of tunneling by heavy molecules is surprising, yet has shown remarkable consistency with the experimental results. The need for a significant potential energy barrier of more than 1.0 eV (in the case of Fe(111)) to explain the results has been contradictory to nonmolecular beam thermal studies based on crystal temperature effect on the dissociation kinetics.^{12–14} These experiments have been analyzed in terms of a kinetic model (Arrhenius expression) predicting a barrier for dissociation of less than 0.1 eV. Phenomenological kinetic arguments were necessary to explain the extremely small dissociation probability at thermal energies on the order of 10^{-7} – 10^{-6} .¹⁵ Similar lack of consistency between beam experiments and those performed with ambient gas at thermal energies has later been found for the dissociation of nitrogen on another potentially active ammonia synthesis catalyst based on rhenium.^{6,16}

In this study we present the first molecular beam–dissociative chemisorption study of nitrogen on Ru(001). Ruthenium is the most active non-iron ammonia synthesis catalyst.¹⁷ The sticking probability of nitrogen into the *molecular* adsorption well on Ru(001) decreases with increasing kinetic energy.¹⁸ The dissociation of ambient nitrogen molecules on Ru(001)^{19,20} was measured to be *surface temperature independent* with a probability of 2×10^{-6} ^{19a} at low pressures or less than 10^{-12} ^{19b} as deduced from high-pressure studies. The quantum mechanical analysis suggests a unified framework for the dissociation of

N₂ on all three transition metals, Fe(111), Re(001), and Ru(001).²¹ The dissociation mechanism is described by a direct nonadiabatic tunneling from the molecular to the atomic potentials. This model has recently been used to explain the different and opposing crystal temperature effects on the dissociation probability of nitrogen on Fe and Re, including the lack of temperature dependence of S_0 in the case of Ru.²¹

II. Experimental Section

The experiments reported here were conducted in a molecular beam–surface scattering chamber equipped with standard surface cleaning and characterization tools. The base pressure was 1×10^{-10} Torr, rising to 2×10^{-8} Torr when the beam is on. The supersonic beam has been generated in a differentially pumped section composed of three chambers, separated by a skimmer and two collimating apertures. A ceramic nozzle with an orifice of 100 μm could be heated to 1850 K.²² A 400 Hz chopper on a compact synchronous motor in the second chamber was used for time of flight measurements to determine the velocity distributions of the incident nitrogen molecules seeded in He or in H₂. The most probable velocity was used to define the incident kinetic energy, and from the width of the distribution an energy spread $-\Delta E/E \approx 0.25$ was deduced. The beam size at the crystal position is somewhat larger than the sample, ensuring a homogeneous distribution of nitrogen atoms on the surface. This enabled the use of temperature-programmed desorption (TPD) to monitor the number of atoms on the surface, with sensitivity down to 1×10^{-3} of the saturation molecular N₂ coverage at a surface temperature of 95 K, considered to include $(5.5 \pm 1) \times 10^{14}$ molecules/cm².²³ Ar⁺ ion sputter at 600 V followed by oxygen treatment and then annealing at 1600 K resulted in very sharp LEED spots with the proper hexagonal symmetry. Cleanliness was determined by Auger spectroscopy. The surface temperature during exposure to the beam was kept at 600 K to avoid any contamination by background gases (mostly water and CO) or by the H₂ carrier gas. Steady state coverage of H atoms during exposure to the beam at a crystal temperature of 600 K is estimated to be less than 10^{-4} of the saturation hydrogen coverage obtained at surface temperatures below 250 K. This negligible H coverage was found to have no effect on the dissociation probability. We reached this conclusion by changing the crystal temperature in the range 500–600 K with N₂ in a beam having H₂ as the carrier gas.

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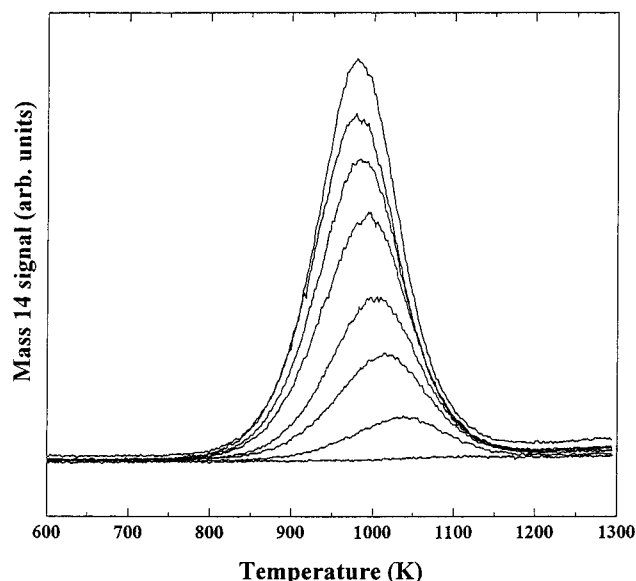


Figure 1. Recombinative desorption of N_2 (QMS at mass 14) following exposure of Ru(001) at 600 K to a beam of 2% N_2 in He at 2.2 eV kinetic energy. Exposure times are 0 s (background, bottom curve) to 200 s (top curve).

Low probability dissociative chemisorption runs in which exposure times exceeded 5000 s (kinetic energies below 1 eV) were performed with the ion gauge filament off. This is due to the measurable contribution of stray electrons to the dissociation of N_2 via electron-stimulated processes. This effect was reported previously by Shi et al.^{19b}

III. Results and Discussion

Dissociation probabilities were determined from the initial (linear) slope of coverage vs exposure curves. The flux of nitrogen molecules in the beam was $(10 \pm 3) \times 10^{13}$ molecules \cdot cm $^{-2}$ s $^{-1}$ for a typical seeding of 2% molecular nitrogen in He or H_2 . The relative number of dissociating molecules was obtained from the area under the TPD peak of the recombinative desorption of nitrogen. Typical TPD spectra following exposure of Ru(001) at 600 K to a beam of N_2 molecules having 2.2 eV kinetic energy are shown in Figure 1. The area under these peaks was then normalized to the area under the TPD peak obtained from saturation coverage of the molecular nitrogen near 114 K. The known density of N_2 molecules at saturation coverage,²³ enables one to obtain the dissociative sticking probability (S_0) after division of the relevant density from the TPD area by the incident N_2 beam exposures.

Because of the use of TPD for the determination of S_0 and the low values of S_0 at kinetic energies below 1 eV, it was important to assess the potential contribution of subsurface nitrogen to the observed TPD signal. The importance of these species in the case of iron surfaces has been discussed extensively.²⁴ Subsurface nitrogen in the case of Ru(001) was prepared by exposing the surface to 10^6 langmuirs of high-purity ambient N_2 at a crystal temperature of 600 K. When the base pressure returned to its initial level, the surface was flashed to remove all adsorbed atomic nitrogen. Then the crystal temperature was raised again to 600 K for a period of time (15 000 s) equivalent to the longest exposure time to the beam. TPD following this procedure defines the maximum possible contribution to the atomic adsorbate population from subsurface nitrogen as a result of diffusion from the bulk. A signal equivalent to that obtained after 25 s exposure time to a beam at 2.2 eV kinetic energy was recorded (see Figure 1, second curve from bottom). Assuming linearity in time, the appropriate

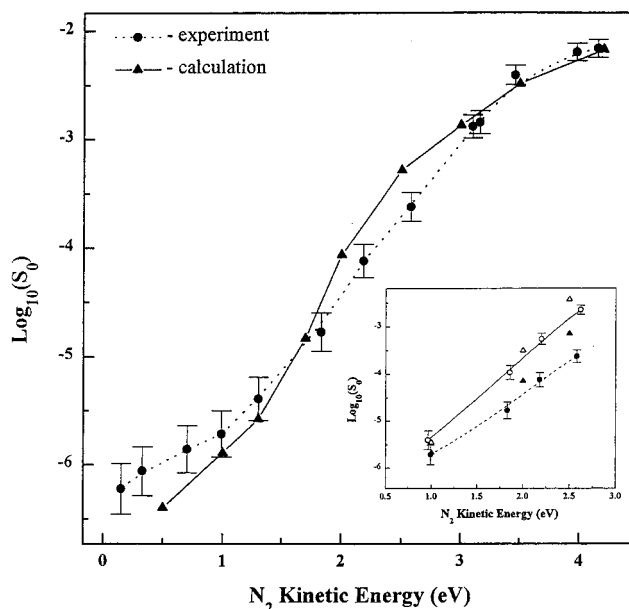


Figure 2. Dissociative sticking probability (S_0) of N_2 on Ru(001) as a function of incident kinetic energy. Filled circles and triangles represent the molecular beam experimental results and calculations, respectively, for nozzle temperatures below 700 K. The open circles and triangles represent the experiment and theory, respectively, for a nozzle temperature of 1750 ± 100 K, which include vibrationally excited molecules (see insert). The solid and broken lines in the inset are guides to the eye through the experimental data points.

subtraction was made at the longest exposure times when this effect could contribute more than 5% of the TPD signal.

Another background measurement was done with the beam on but the surface turned 90° away from the normal position in front of the beam. This procedure determines the minor contribution to dissociative adsorption from the thermal background gas. These background contributions and in particular the subsurface atoms amount to about 3×10^{-3} of the saturation molecular nitrogen coverage. This can be a significant contribution in the case of low kinetic energy experiments, e.g. 50% of the area obtained from nitrogen molecules at 0.15 eV exposed for 15000 s.

The corrected initial dissociative sticking probability (S_0) of nitrogen molecules as a function of kinetic energy at an incident angle normal to the surface is presented in Figure 2. Measurements were taken at several different seeding levels, with two carrier gases (He and H_2) and a range of nozzle temperatures up to 1850 K. Three distinct regions of interest are found in Figure 2. At the high kinetic energy range above 3.5 eV, a saturation-like behavior of S_0 is observed with values approaching 10^{-2} . This behavior is similar to the previous experiments of this kind on W(110),³ Fe(111),⁴ and Re(001).⁹ In the second region between 1.0 and 3.5 eV, S_0 increases exponentially with incident kinetic energy. Finally, at the low energy regime below 1.0 eV the slope decreases again, approaching a value of $(5 \pm 2) \times 10^{-7}$ at a kinetic energy of 0.15 eV.

The shape of curves of S_0 vs kinetic energy has been discussed in terms of a tunneling mechanism in the case of the dissociation dynamics of hydrogen and deuterium on Cu(111).²⁵ Classical models, on the other hand, would predict that for incident kinetic energies above or below an effective barrier for dissociation S_0 should approach unity or vanish, respectively. Rotation of the incident molecules was found to reduce the saturation level of S_0 from unity to 0.6–0.7,²⁵ but never as low as reported here ($S_0 \approx 10^{-2}$). Alternatively, a classical picture based on a wide distribution of barrier heights has been used to generate an "S" shape for S_0 vs kinetic energy curves.³ It is often difficult,

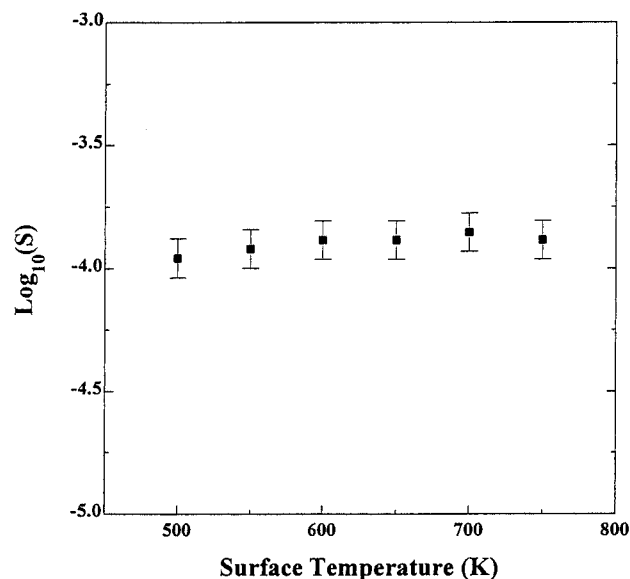


Figure 3. Dissociative sticking probability (S_0) of N₂ in a beam having 2.5 eV incident kinetic energy as a function of crystal temperature.

however, in these models to explain the physical origin of the width of the distribution of barriers.

We have studied the crystal temperature (T_s) effect on S_0 . At a kinetic energy of 2.5 eV we have performed measurements for several values of T_s in the range 500–750 K, as shown in Figure 3. Within experimental uncertainty, there was no effect on the dissociation probability. The same results were obtained at lower and higher kinetic energies. Similar observations were also reported for ambient N₂ dissociation on the same surface.^{19a} The lack of crystal temperature effect on S_0 has been predicted theoretically for the entire range of kinetic energies,²¹ as will be discussed below.

The role of vibrational excitation on the dissociation dynamics is an important ingredient for understanding the dissociation mechanism. Moreover, it provides fine details on the topology of the potential energy surfaces which govern the dissociation dynamics. Vibrationally excited molecules were generated by changing the nozzle temperature. In the kinetic energy (E_k) range 1.0–2.6 eV, pairs of measurements were performed at the same E_k : In each pair one of the measurements was done with He as a carrier gas at high nozzle temperature and the other with H₂ at lower nozzle temperature. Under conditions of continuous supersonic beam expansion it is usually assumed that there is no significant excitation of rotational degrees of freedom. Vibrational excitation, on the other hand, follows the nozzle temperature with hardly any relaxation during the expansion through the nozzle.⁵ For example, with the nozzle at 1850 K the beam contains 16.2% nitrogen molecules at $v = 1$ and 2.7% at $v = 2$.²⁶ By changing the level of vibrational excitation in the beam for the same E_k , we could study its effect on S_0 , as was done before.^{5,6} The effect of residual hydrogen atoms coverage on the surface at 600 K in the cases where hydrogen was the carrier gas was checked to be totally below our detection limit, as mentioned in the Experimental Section. Consistently for all four pairs of measurements performed at $E_k = 1.0, 1.8, 2.2$, and 2.6 eV, the beam with higher density of vibrationally excited molecules (N₂ seeded in He) has shown significantly larger reactivity. In addition, the difference between the hotter and colder beams becomes larger as the kinetic energy increases. This is shown in the inset of Figure 2.

A simple analysis of the extent of enhancement of S_0 due to vibrational excitation proceeds as follows: We wish to assess

the relative efficacy of vibration vs translation in enhancing dissociation. The energy content of the first two excited vibrational quantum states, $v = 1$ and $v = 2$, of N₂ in the gas phase is 0.289 and 0.574 eV, respectively. If for the same fraction of vibrationally excited molecules (as in the beam) this energy is fully transformed into translation, the relative importance of these two degrees of freedom can be estimated and compared. For example, at a kinetic energy of 2.2 eV and a nozzle temperature of 700 K, raising the nozzle temperature to 1850 K and converting the vibrational to translational energy (taking into account the actual fraction of the beam that is vibrationally excited) results in a rather small change of S_0 from $10^{-4.2}$ to $10^{-4.0}$. The experimentally determined change of S_0 at the above conditions of the beam is from $10^{-4.2}$ to $10^{-3.3}$, which is almost an order of magnitude larger. Faster dissociation rates of vibrationally excited molecules have been observed for all other incident kinetic energies, as discussed in the previous paragraph. The faster rates become even more pronounced as the kinetic energy increases, as seen in the inset of Figure 2.

It is concluded that in contrast to other systems (N₂ dissociation on Fe(111)⁵ and on Re(001)⁹), the vibrational degree of freedom of N₂ is *more efficient* than translation in penetrating through the barrier for dissociation on Ru(001). The relative importance of the two degrees of freedom is kinetic energy dependent.

Details of the theoretical aspects of the nonadiabatic tunneling model have been described before.^{7–9,21} Briefly, a direct dissociation mechanism is assumed, based on a the following quantum nonadiabatic picture: A gas phase nitrogen molecule approaches on the molecular (physisorption, V_{phys}) potential energy surface (PES) and crosses to the atomic (chemisorption, V_{chem}) PES while dissociating. Crossing between the two PES's becomes possible due to the nonadiabatic coupling potential, $V_{\text{int}}(z, r)$. The forms of the potentials are

$$V_{\text{phys}}(z, r) = V_{\text{N}_2\text{-M}}(z, r) + V_{\text{N}_2}(z, r) \quad (1)$$

$$V_{\text{chem}}(z, r) = V_{\text{N-M}}(z, r) + V_{\text{N-N}}(r) \quad (2)$$

$$V_{\text{int}}(z, r) = C_b F(r) G(z); F(r) = \exp[-\gamma_r(r - r_i)^2]; \text{ and } G(z) = \exp[-\gamma_z(z - z_i)^2] \quad (3)$$

The explicit forms of the potentials used in the calculations are summarized in Table 1.

For energies below the nonadiabatic crossing seam between the two PESs, which is empirically set at 2.2 eV for the current system, the reaction can be classified as a *tunneling* event. A contour plot of the PESs and a one-dimensional cut in the resulting 2D potential is shown in Figure 4. The experiments were simulated by solving the time dependent Schrödinger equation using two degrees of freedom: the N–N distance, r , and the nitrogen–surface distance, z . The method is similar to the one recently used to study the surface temperature effect on the dissociation dynamics of N₂ on Fe, Re and Ru.²¹ The parameters used for the dynamical simulations are given in Table 2. The main modification needed for the calculations performed here specifically for the N₂/Ru(001) system was the adjustment of the nonadiabatic coupling potential (V_{int}) and the height of the minimum crossing point between the two PESs, which defines the effective activation barrier. To save computational effort, the surface motion was frozen in the present calculation. As a result, the surface recoil effect, which has previously been studied in detail,^{27,28} has not been accounted for. The resulting theoretical curve of S_0 vs kinetic energy is therefore somewhat

TABLE 1: Potential Parameters

$\hat{V}_{N_2-M}(r,z) =$ $D_{N_2-M}(e^{-\alpha_{N_2-M}(z)} - (C/z^3)(1 - \Gamma_4(z,\alpha)))$ $\Gamma_4(z,\alpha) = \sum_{k=0}^4 (n(z-z_0)^k/k!) e^{-\alpha(z-z_0)}$ $\hat{V}_{N_2}(r,z) = D_{N_2}(1 - e^{-\alpha_{N_2}(z)(r-r_e)^2})$	$\hat{V}_{N_2-M}(z,r)$ $D_{N_2-M} = 0.245 \text{ eV}$ $D_{N_2} = 9.74 \text{ eV}$	$\alpha_{N_2-M} = 3.8 \text{ \AA}^{-1}$ $C = 0.18$ $\alpha_{N_2} = 2.68 \text{ \AA}^{-1}$ $r_e = 1.1 \text{ \AA}$
$\hat{V}_{N-M} = D_{NM}(1 - e^{-\alpha_{N-M}(z-z_e)^2})$ $z_e = z_e^{as} - (z_e^{as} - z_e^{ad})\Gamma_4(r,a)$ $\hat{V}_{N-N} = A_d e^{-\alpha_d r}$	$\hat{V}_{N-M}(z,r)$ $D_{N-M} = 6.12 \text{ eV}$ $A_d = 5.8523 \text{ eV}$	$\alpha_{N-M} = 0.845 \text{ \AA}^{-1}$ $z_e^{ad} = 1.54 \text{ \AA}, z_e^{as} = 1.8 \text{ \AA}$ $\alpha_d = 1.2 \text{ \AA}^{-1}$
$\hat{V}_{int}(z,r) = C_b e^{-\gamma_r(r-r_i)^2} e^{-\gamma_z(z-z_i)^2}$	$\hat{V}_{int}(z,r)$ $C_b = 0.0132 \text{ eV}$	$\gamma_z = 3.3 \text{ \AA}^{-2}$ $z_i = 1.63 \text{ \AA}$ $\gamma_r = 2.6 \text{ \AA}^{-2}$ $r_i = 1.1 \text{ \AA}$

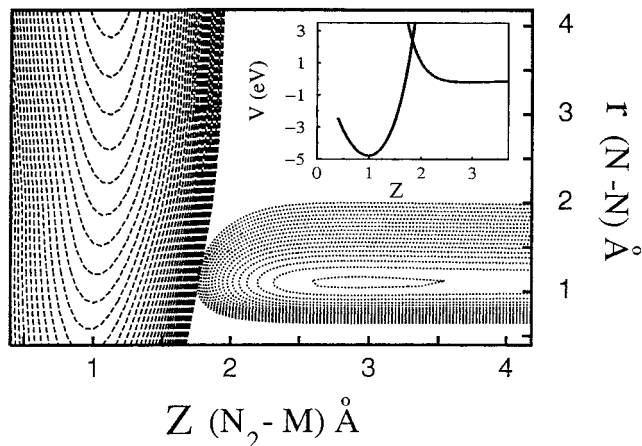


Figure 4. Contour map of the molecular-metal (physisorption) and the atomic-metal (dissociative chemisorption) diabatic potential energy surfaces on which the dynamical calculations were performed. In the inset a one-dimensional cut of the two potentials along the z direction at the equilibrium N-N gas phase separation demonstrates the effective barrier for dissociation of 2.2 eV.

TABLE 2: Typical Grid and Propagation Parameters

$n_z = 64$	$n_r = 64$
$\Delta z = 0.08 \text{ \AA}$	$\Delta r = 0.08 \text{ \AA}$
$z_0 = 1.2 \text{ \AA}$	$r_0 = 0.45 \text{ \AA}$
$N_{ch} = 64^a$	$\Delta t = 10 \text{ au}$

^a Order of Chebychev expansion.

too steep and predicts higher dissociation probabilities. We expect that if the recoil is explicitly taken into account, a more moderate curve and a slightly lower effective barrier will result.

Figure 2 shows the calculated dependence of S_0 on the incident kinetic energy of nitrogen molecules (filled triangles) superimposed on the experimental results. The calculated results reproduce the exponential increase of S_0 and its approach to saturation above a kinetic energy of 3.5 eV reasonably well. At the same time, the surface temperature, which was previously predicted to have no effect on the dissociation event in the case of Ru,²¹ is found to be in line with the experimental results shown in Figure 3.

A very weak translational to vibrational coupling is expected during the collision of N₂ on Ru(001). This is evident by the very small change in the fundamental vibrational frequency of the adsorbed molecule compared with its value in the gas phase.²⁹

The vibrational enhancement, therefore, must result from the shape of the atomic PES, which is slightly curved, as seen in Figure 4. The calculated effect of vibrational excitation is shown in the inset of Figure 2, together with the experimental

results. The simulations reproduce very well the increased importance of vibrational excitation as the kinetic energy increases, a unique feature of the topology of the PES.

Below kinetic energies of 0.5 eV the quantum simulations become less reliable. In the present calculation the wave packet is observed to be trapped in the physisorption well for very long periods of time. This gives a chance for other degrees of freedom to partition the energy and thus increase the residence time even further. Qualitatively when the incident kinetic energy is reduced, the dissociation probability is influenced by the competition between longer residence time and the higher tunneling barrier. As a result at low energies the dissociation probability will fluctuate around its value near an incident energy of 0.5 eV, $S_0 \approx 10^{-6}$. This generates the familiar "S" shape for the dissociation as a function of kinetic energy involving the tunneling mechanism, which is also observed experimentally, as shown in Figure 2.

An important check of the validity of the quantum mechanical tunneling model is to estimate a possible contribution to dissociation from nitrogen molecules in the high energy tail of the kinetic energy distribution in the beam. We have simulated our incident beam by fitting a Gaussian distribution of kinetic energies, which nicely fits the experimental data. We then assigned a unity dissociation probability for every molecule with kinetic energy above the effective barrier of 2.2 eV. It was found that for incident beam energies below 1.4 eV the fraction of molecules possessing more than 2.2 eV is less than 10^{-10} . This fraction very rapidly increases by more than 8 orders of magnitude between 1.5 and 2.5 eV, reaching unity dissociation probability for incident energies above 2.75 eV. The obvious severe deviation of these simple classical calculations from the experimental results rules out a simple classical explanation for the experimental results.

A central feature of the nonadiabatic quantum mechanical model is its prediction of the plateau in the S_0 vs kinetic energy plot at high energies, which typically is significantly less than unity probability (in this study it is found to approach 10^{-2}). Our understanding of tunneling by relatively heavy atoms and molecules like nitrogen, strongly relies on details of the potential energy surfaces. In the system of N₂/Ru(001), as in the case of CH₄ on various metals, the barrier for dissociation has been suggested as a rather narrow one; see Figure 4. Assuming this description correctly explains the PES, tunneling is a natural physical consequence that should take place, as shown in the present calculations. Moreover, it is important to emphasize that the value of the plateau, $S_0 \approx 10^{-2}$, for the N₂/Ru(001) system cannot be derived or be reproduced by any of the adiabatic theoretical approaches.²⁵ The importance of the present theoretical framework is, therefore, in providing a unique tool to obtain some information on the nonadiabatic coupling

potential ($V_{\text{int}}(z,r)$ in Table 1) between the molecular and the atomic potentials.

To conclude, the N₂/Ru(001) system has the same dissociative chemisorption dynamics characteristic of the nitrogen-transition metal family. Its remarkable barrier height of 2.2 eV shifts and spreads the "S"-shaped dissociation probability curve to high kinetic energies. It is interesting to mention a very recent theoretical study based on a completely different approach of the density functional calculations, which predicted for the nitrogen-ruthenium system a barrier for dissociation of 1.8 eV,³² which is remarkably close to the value found in this study. Moreover, with the surface recoil taken into account the agreement is expected to be improved even further. This system is unique in the role of vibration in the enhancement of the dissociation event, being much more efficient than in the case of N₂ dissociation on Fe(111) or on Re(001).

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