

Effect of molecular energy content on the dissociative chemisorption of N_2 on $Re(0001)$

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Dissociative chemisorption dynamics of N_2 on $Re(0001)$ was studied by employing molecular-beam methods. The dissociation probability S_0 increases three orders of magnitude from 4×10^{-5} to 4×10^{-2} upon increasing the normal translational energy of N_2 from 0.05 to 1.5 eV, respectively. These results imply the presence of a barrier for dissociation of 0.6 ± 0.15 eV. The influence of vibrational excitation of the incident molecules on S_0 was investigated. A quantum-mechanical study was carried out to simulate the dissociation dynamics. The calculated results reproduce the experimental S_0 dependence on translational energy over a wide range. The vibrational energy is predicted to be less effective for the enhancement of S_0 , in agreement with experiment. The quality of the agreement between the theoretical simulation and the experimental data strongly supports a tunneling process through the adiabatic barrier for dissociation as a key mechanism to explain the dynamics of N_2 chemisorption over Re .

1. Introduction

The dissociation of nitrogen molecules on metal surfaces is a fundamental surface process, in particular due to its relevance to the industrial ammonia synthesis. Over iron catalysts, the process has been shown to be the rate-limiting step of the entire complex ammonia synthesis from the gas mixture N_2 and H_2 at high pressures [1–3]. Similar results were obtained over model rhenium single-crystal catalysts as well [4]. This is the motivation for extensive study of the kinetics of adsorption and desorption of N_2 and its dissociative chemisorption on iron [2,5] and rhenium [6]. New insight into the dynamics of the dissociation event, has been found by the application of molecular-beam/surface-collision methods [7–10], which enable control of the incident kinetic energy of the collider. This is an experimental simulation of the high-pressure industrial conditions.

The dissociation of N_2 on $Fe(111)$ was studied experimentally [7,8]. It was found that the dissociation

probability (S_0) increased by five orders of magnitude when the incident kinetic energy increased from 0.1 to 2 eV and above [7]. The relative importance of the vibrational and translational energies was also addressed in the above system [8] where the vibrational degree of freedom was shown to be less efficacious than the translation. The detailed dynamics of this system and that of N_2 on $Re(0001)$ were also considered theoretically, by applying quantum-mechanical [9,10] and classical [11,12] approaches to simulate the dissociation event over model potential energy surfaces (PESs). The quantum-mechanical treatment strongly suggests that the dissociation of N_2 over $Fe(111)$ as well as on $Re(0001)$ proceeds via a nonadiabatic tunneling mechanism through a relatively high effective energy barrier.

In this paper, we report the first experimental molecular-beam surface-collision study of N_2 on $Re(0001)$. It was found that by increasing the (normal) translational energy from 0.05 to 1.5 eV, the initial (zero coverage) dissociative sticking probability (S_0) rose from 4×10^{-5} up to 4×10^{-2} at a crystal temperature of 830 K. The effect of vibrationally excited N_2 molecules in the incident beam,

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achieved by heating the nozzle, was examined. The results are fitted and discussed in terms of the model quantum-mechanical calculations which were previously reported [10]. A new PES has been constructed and was found to fit the experimental results for Re(0001).

2. Experimental

The ultra-high vacuum (UHV) high-pressure chamber, the crystal handling and the temperature-programmed desorption (TPD) procedures were described elsewhere [6]. Here, we shall discuss a few details that are pertinent to the beam experiments. A single stage of differential pumping connects a continuous ceramic-nozzle [13,14] source chamber to the UHV at a fixed incident angle of 50° below the horizontal plane of the chamber. Due to pumping speed constraints, the pressure behind the 80 μm diameter nozzle was typically 100 Torr at room temperature. In order to compensate for the reduced flux, the nozzle to sample distance is relatively short – 16.5 cm. The 0.7 mm diameter nickel skimmer at the entrance of the differential pumping section and a 3 mm diameter orifice at the entrance to the UHV chamber, generate a molecular beam which covers the entire sample area at the center of the chamber. The flux of N_2 molecules at the sample was estimated to be $(2 \pm 1) \times 10^{14}$ molecules $\text{cm}^{-2} \text{s}^{-1}$ for a 3% N_2 beam in a He carrier gas. The details of this and other estimates will be given elsewhere [15].

A significant increase of the pressure in the UHV chamber occurs when the beam shutter is open (from 5×10^{-10} to 2×10^{-7} Torr). Therefore, every exposure of the sample to the beam is actually composed of two separate measurements: one with the sample facing the beam and the second with identical exposure time but with the sample rotated 90° away from the beam. Each such measurement is preceded by a 1 min Ar^+ sputter and annealing and a TPD run following the exposure to the beam. By subtracting the TPD area under the recombinative desorption peak near 1100 K, obtained with the sample rotated away from the beam, the net effect of the beam is obtained. A pair of measurements of this kind is shown in fig. 1, for an exposure time of 4 s at incident energy of 0.5 eV. This area is normalized to the

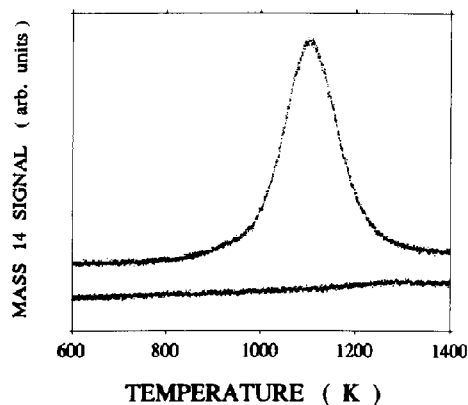


Fig. 1. TPD spectra following the exposure of Re(0001) at 830 K to the molecular beam (3% N_2 in He) at normal translational energy of 0.75 eV for 4 s (upper spectrum). The lower spectrum is obtained following the same procedure, but with the sample rotated 90° away from the beam, to evaluate the background contribution to the dissociation.

area under the saturation physisorbed N_2 molecules^{#1} and then divided by the incident flux. From the slope of coverage versus exposure plot at zero coverage the initial dissociative chemisorption probability S_0 is determined. It was found necessary to expose the Re(0001) sample to 10^5 langmuir of N_2 prior to the beginning of these experiments. This was done in order to minimize N diffusion to the bulk. Careful check of the effect of such exposure on the TPD spectra was done by employing isotope scrambling measurements between bulk and surface ^{15}N and ^{14}N atoms. We found a contribution to the TPD of about 20% from bulk atoms at the lowest coverages (smallest S_0), decreasing to less than 1% at high coverages (large S_0). We found the TPD to be a more sensitive and reproducible method for nitrogen-coverage determination on Re(0001) than Auger spectroscopy.

The kinetic energy of the impinging nitrogen molecules was estimated from the seeding and nozzle-temperature conditions [18]. Direct time-of-flight measurements of the incident N_2 molecules could not be applied in the current experimental setup. These kinetic energy estimates, which sensitively depend

^{#1} The area under the saturation physisorption peak is compared to the saturation CO coverage. The CO saturation coverage was previously discussed [16,17] and is estimated to be $(6 \pm 2) \times 10^{14}$ molecule/ cm^2 .

on the accuracy of the nozzle-temperature measurement, are taken as upper-bound values for the actual energies. The velocity distribution of a seeded beam at pressures behind the nozzle of 100 Torr at similar conditions to those in the present study have been reported to correlate with a Boltzmann distribution at 40 K [14].

Finally, the unique combination of a molecular beam and a high-pressure capability in the same apparatus (up to 1 atm) allows for a direct comparison of model UHV studies with realistic high-pressure experiments.

3. Results and discussion

3.1. Experimental

The beam in the current experimental setup strikes the surface at a fixed incident angle of 40° . We are unable, therefore, to determine experimentally whether, for the $\text{N}_2/\text{Re}(0001)$ system, S_0 scales with normal energy or whether it scales with the total energy, namely independent of incident angle, as was found in the $\text{N}_2/\text{W}(110)$ system [19,20]. We have chosen to present our data as if it obeys the normal energy scaling, as was found for most gas-surface systems [22–25].

The variation of S_0 with incident normal translational energy ($E_n = E_i \cos^2 \theta$, E_i is the total incident translational energy of N_2 and $\theta = 40^\circ$) is shown in fig. 2 for a fixed crystal temperature of 830 K. This temperature was chosen in order to minimize the coadsorption of background molecules like H_2 and CO at the time of exposure of the sample to the beam. The coadsorption of CO was previously reported to decrease drastically the dissociation of N_2 on rhenium [21]. The value of S_0 increase from $(4 \pm 2) \times 10^{-5}$ at $E_n = 0.05$ eV to $(4 \pm 1) \times 10^{-2}$ at $E_n = 1.5$ eV. We observed that the error bar is maximum at the intermediate incident energy of 0.3–0.6 eV, where fluctuations in the value of S_0 are up to a factor of 1.5 from the mean value. At the saturation level, the uncertainty is only 25%, while at the lowest incident energies, S_0 is within 50% of the numbers previously measured with ambient N_2 molecules on $\text{Re}(0001)$ [6]. The lowest translational energy is obtained with a pure N_2 beam at nozzle temperature

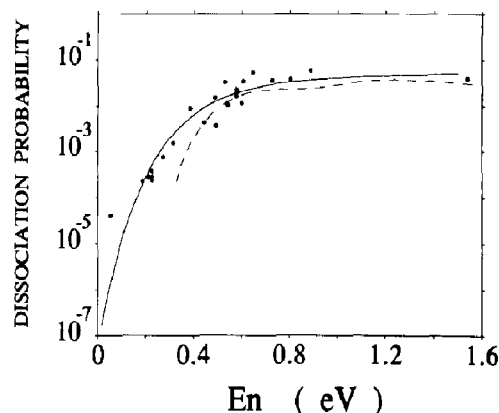


Fig. 2. The dissociation probability S_0 as a function of normal translational energy of the impinging N_2 molecules. The points are experimental data and the solid line is obtained from the quantum-mechanical simulation for $v=0$ described in the text (see also table 1). The dashed line represents the $v=1$ initial condition with E_n shifted by the vibrational energy. The fact that the dashed curve is always lower than the $v=0$ solid curve implies that for this potential, vibration is always less effective than translation when the total energy is the same.

of 300 K. All other translational energies in fig. 2 are obtained with a 3% N_2 in He and a range of nozzle temperatures between 300 and 1170 K. The highest kinetic energy was obtained by seeding in H_2 at a nozzle temperature of 900 K. An exponential increase of S_0 is evident at low translational energies and a saturation-like behavior for energies above 0.6 ± 0.15 eV. The dissociation probability S_0 is practically constant for $E_n > 0.8$ eV. A similar change of S_0 with E_n was previously found for the dissociation of N_2 on $\text{Fe}(111)$ [7].

The saturation-like shape of S_0 above a given translational energy is usually considered as an indication of a barrier for dissociative chemisorption. The data in fig. 2 imply the presence of a barrier for chemisorption in the N_2 - $\text{Re}(0001)$ system of the order of 0.6 ± 0.15 eV. A quantum-mechanical simulation of the data is given below.

A central question regarding the dissociation dynamics is the relative importance of the translational and internal energy of the impinging molecules on S_0 . As has been shown in a model quantum-mechanical study [10], this experimental input has direct bearing on the details of the potential energy surface, which govern the dissociation dynamics. An

attempt to address this point experimentally was made by increasing the nozzle temperature, yet keeping the translational energy constant by appropriate seeding conditions in the beam. For a pure N_2 beam at 1280 K, the normal translational energy of 0.22 eV is the same as that of 3% N_2 in He at 300 K. However, since the vibrational cooling is rather inefficient during the expansion through the nozzle, it has been estimated [8] that the vibrational population in the beam is at a Boltzmann distribution at the nozzle temperature. This is, of course, an upper-limit estimate and the actual vibrational population should reflect a lower temperature. This is due to partial collisional deactivation of vibrationally excited molecules during the expansion. However, as experimental measurements show [26], the vibrational temperature is remarkably close to the nozzle temperature. Vibrational deactivation by the metal a few angstroms away from the surface may also occur [27]. It is not clear to what extent this process may quench the vibrationally excited molecules before the collision becomes effective. Data from other systems (CO and CO_2 on silver [27]) suggest that 30–80% of the vibrationally excited molecules will survive a single collision, depending on the vibrational mode and surface temperature. In the case of NO ($v=1$) scattered from silver, survival probabilities of 0.9 were reported [28]. If we take the nozzle temperature at 1280 K as determining the vibrational population and neglecting the population at $v=2$, we have 7.2% of the impinging molecules at $v=1$, the rest at the ground vibrational state.

It was found that the overall dissociation probability for $E_n=0.22$ eV increased from $S_0=4\times 10^{-4}$ to 10×10^{-4} by increasing the vibrational population at nozzle temperature of 1280 K. A similar experiment was performed with a seeded beam of 7.5% N_2 in He at a nozzle temperature of 1032 K. Under these conditions at $E_n=0.18$ eV, we found that the dissociation probability increased from 1.1×10^{-4} for the seeded beam to 2.2×10^{-4} for the pure N_2 at higher nozzle temperature.

Due to the level of uncertainty in the absolute values of S_0 , seen in fig. 2, we are unable to extract meaningful dissociation probabilities for each of the vibrational states separately. However, we may conclude from the data, that the vibrational degree of freedom is somewhat less important than the trans-

lation for the enhancement of S_0 . This conclusion is based on the following analysis of the data: Assume we can add 0.289 eV (the vibrational energy content at $v=1$) to the translational energy of 7.2% and 3.8% of the impinging N_2 molecules, which is the corresponding population of vibrationally excited molecules at nozzle temperatures of 1280 K ($E_n=0.22$ eV) and 1032 K ($E_n=0.18$ eV), respectively. According to fig. 2, such a mixture is expected to yield $S_0=1.1\times 10^{-3}$ and $S_0=4.1\times 10^{-4}$ for the two nozzle temperatures. Consider the expected wider translational energy distribution at the high nozzle temperatures, we may conclude that the observed dissociation probabilities of $S_0=1.0\times 10^{-3}$ and $S_0=2.2\times 10^{-4}$ at the nozzle temperatures of 1280 and 1032 K, reflect somewhat less effective enhancement due to vibrational excitation of the impinging nitrogen molecules. This conclusion is in a qualitative agreement with the results of the theoretical simulation presented below.

Finally, a "high pressure" exposure of the Re surface (5–50 mTorr for 10 s) which is equivalent to about 10^6 s of molecular-beam exposure time, was performed. It was found that the saturation coverage reached by the more energetic beam molecules is higher. The exact reason for this difference is not clear, and deserves further investigation.

3.2. Theoretical simulations

The physical picture used for the simulation is a quantum-mechanical wavepacket motion from the physisorption (N_2 -metal) PES (V_1) bifurcating to the chemically bound N-metal PES (V_2). The basic simulation technique has been described previously [10]. The main change is a modified potential energy surface.

The first step in the theoretical investigation is the definition of the interaction potential. To approach this problem, all available knowledge of the system has to be employed. The accuracy of ab initio electronic structure calculations is not good enough to obtain a reliable potential surface, in particular because the system also includes excited electronic states and not only the ground adiabatic surface. Most experimental measurements on the system provide asymptotic data on certain limits of the potential. The strategy chosen to construct the potential is basically

empirical. As was mentioned previously [10,30], the reaction takes place on more than one potential energy surface. First to be considered is the asymptotic N_2 -metal interaction, V_1 . Because the long-range interaction stems from polarization, it has an inverse cubic dependence on the molecule-surface distance, z (see table 1). For the short-range interaction, an exponential repulsion form is chosen, $Ae^{-\alpha z}$. A switching function is used to turn-off the polarization term at short distances. A smooth function of this kind is the incomplete gamma function which was adopted here [30]. The potential parameters are fitted to known experimental data on the molecular-metal vibrational frequency and physisorption well-depth [10]. The consistency of these parameters is checked by relating them to scaling laws of Ihm et al. [31] which enable the comparison of gas-phase polarization measurements to surface interactions. As

for the molecular vibration, a smooth function interpolating the gas-phase vibrational frequency to the one measured on the surface is used.

For the N-metal PES (V_2), the well-depth and basic vibrational frequencies and equilibrium distances were adapted from similar systems [10]. These values are used to determine the Morse-potential parameters for the N-metal bond. The nitrogen-nitrogen repulsive potential is described asymptotically by a repulsive interaction, the term c_2/r^2 . This parameter is estimated by fitting TPD experiments [6]. Nitrogen-nitrogen interaction at short interatomic separation is modeled by a repulsive exponential term. The potential form and the relevant parameters are summarized in table 1. The main difference of this potential from the one used previously [10] is a longer-range attractive part in the N_2 -metal PES. Since the well-depth of the two potentials

Table 1
Parameters of potential, grid and time step

Potential parameters

molecular-metal PES

$$V_1(z, r) = Ae^{-bz} - \frac{c}{z^3} (1 - \Gamma(z, 0, b)) + D_{N-N} (1 - \exp\{-\alpha_{N-N}(z) [r - r_e(z)]\})^2 - D_{N-N}$$

$$\alpha_{N-N}(z) = \alpha_{N-N}^{\text{ad}}, r_e = r_e^{\text{ad}}, \text{ for } z < z_e$$

$$\alpha_{N-N}(z) = \alpha_{N-N}^{\text{ns}} - (\alpha_{N-N}^{\text{ns}} - \alpha_{N-N}^{\text{ad}}) \Gamma(z, z_e, b) \text{ for } z > z_e$$

$$r_e(z) = r_e^{\text{ns}} - (r_e^{\text{ns}} - r_e^{\text{ad}}) \Gamma(z, z_e, b)$$

$A = 3.07 \times 10^5 \text{ kJ/mol}$	$b = 4.23 \text{ \AA}^{-1}$	$c = 117.98 \text{ kJ \AA}^3/\text{mol}$
$D_{N-N} = 943.2 \text{ kJ/mol}^{\text{a)}$	$\alpha_{N-N}^{\text{ns}} = 2.67 \text{ \AA}^{-1 \text{ a)}$	$z_e = 2.45 \text{ \AA}$
$r_e^{\text{ns}} = 1.098 \text{ \AA}$		$\alpha_{N-N}^{\text{ad}} = 2.48 \text{ \AA}^{-1 \text{ a)}$
		$r_e^{\text{ad}} = 1.100 \text{ \AA}$

atom-metal PES

$$V_2(z, r) = D_{NS} \{1 - \exp[-\alpha_{NS}(z - z_e^{\text{NS}})]\}^2 + E \{1 + \exp[-\beta(r - r_e^{\alpha})]\}^2 + \frac{\alpha}{r^2} [1 - \Gamma(r, r_e, \beta)] - D_{NS} - E$$

$D_{NS} = 1206.4 \text{ kJ/mol}^{\text{a)}$	$z_e^{\text{NS}} = 1.6 \text{ \AA}$	$\alpha_{NS} = 0.53 \text{ \AA}^{-1}$
$E = 627.6 \text{ kJ/mol}$	$r_e^{\alpha} = 0.5 \text{ \AA}$	$\beta = 2.7 \text{ \AA}^{-1}$
		$\alpha = 645.3 \text{ kJ \AA}^2/\text{mol}$

$$\text{incomplete gamma function: } \Gamma(x, x_0, a) = \sum_{k=0}^{k=\infty} \frac{[a(x-x_0)]^k}{k!} \exp[-a(x-x_0)]$$

interaction potential

$$V_{1,2}(z, r) = Ce^{-\alpha r} e^{-\alpha z}$$

$C = 18 \text{ kJ/mol}$	$\alpha_r = 0.6 \text{ \AA}^{-1}$	$\alpha_z = 0.7 \text{ \AA}^{-1}$
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Typical grid parameters

initial coordinate position	$z_0 = 0.9 \text{ \AA}$	$r_0 = 1.0 \text{ \AA}$
grid spacing	$\Delta z = 0.01955 \text{ \AA}$	$\Delta r = 0.0125 \text{ \AA}$
number of points in molecule-metal grid	$N_z = 288$	$N_r = 48$
number of points in atom-metal grid	$N_z = 96$	$N_r = 144$
Chebyshev time propagation		
propagation time step	$\Delta t = 0.02 \text{ ps}$	
number of time steps	$N_t = 18$	

^{a)} Parameters determined from experimental values.

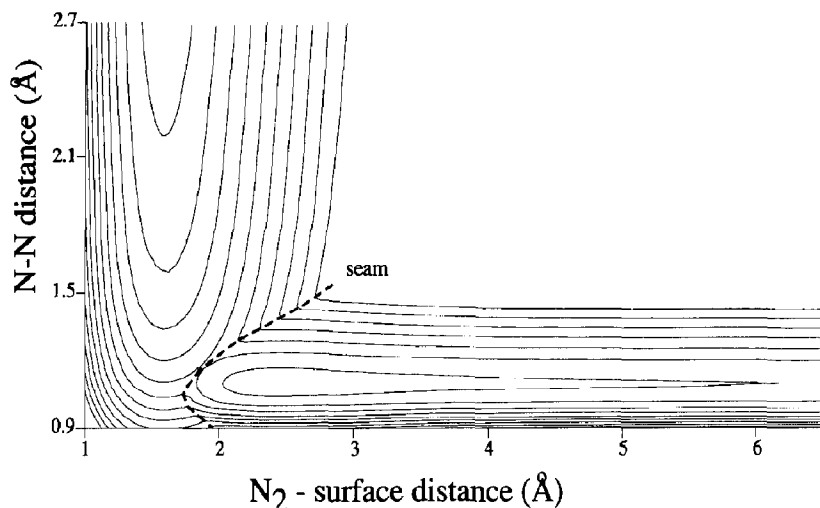


Fig. 3. The adiabatic ground-electronic PES for the system N_2 on $Re(0001)$. Note the shallow well at the entrance valley reflecting the long-range attractive forces. Also the position of the crossing seam represented by a dashed line is slightly shifted towards larger N-N separations. The energy spacing between adjacent contours is 0.54 eV.

is similar, the new PES contains a steeper repulsive part. Consequently, the position of the crossing seam where V_1 crosses V_2 has been slightly shifted to the exit channel. This enhances the relative importance of the incident vibration on the reaction probability. A contour map of the potential can be viewed in fig. 3.

Given the PES, a series of wavepackets with different initial translational and vibrational energies were run. The propagation method and the initial conditions are identical to those described previously in detail [10]. The calculated dissociation probability as a function of incident kinetic energy is displayed in fig. 2 (solid line) together with the experimental data points. An exponential increase in dissociation probability is found for low incident kinetic energy and saturates for the higher energy ($E_n > 0.8$ eV).

The potential energy surface of N_2 on $Re(0001)$ has only one molecular well, as evident by TPD [6] and by an unsuccessful low-temperature attempt to find a weakly chemisorbed precursor state [32]. This is in contrast to the $N_2/Fe(111)$ system, in which a second molecular adsorption state was identified and considered to have an important role as precursor for dissociation [7,33].

The similarity between the quantum-mechanical

simulation and the experimental results is very good over a wide energy range. At the very low energies, the experimental S_0 is above the calculated value. The explanation for this discrepancy is that the calculated results presented here were not convoluted with the experimental energy distribution. A convolution of this kind has been performed to test this point with the PES employed in our previous work [21], resulting in an improved fit at low energies.

The effect of vibrational excitation of the colliding molecule on S_0 is found in the calculation to be always lower than having the equivalent energy in translation (see fig. 2, dashed line compared with the solid line). This result is in agreement with the experimental observations. At $E_n = 0.2 \pm 0.02$ eV, the relative enhancement factor is four times higher for translation over vibration. Currently, a complete quantitative comparison between the theoretical simulation and experimental data is impossible. Such a comparison requires further experimental investigation of the relative efficiency of vibration and translation in enhancing S_0 .

4. Conclusions

The good agreement between experiment and the

quantum-mechanical simulation over a wide range of incident kinetic energy, together with the experimentally confirmed isotope effect [10], strongly support the claim of a tunneling mechanism for dissociative chemisorption of N_2 , presented in previous papers [9–12,34].

The dependence of S_0 on E_n for N_2 on Re(0001) is similar to that of N_2 on Fe(111) [7] (see fig. 4). The most significant difference is in the value of S_0 being more than one order of magnitude higher on Re than on Fe at low energies. S_0 saturates at $E_n > 0.8$ eV for Re(0001), while on Fe(111) the saturation is reached only above 2 eV. The asymptotic value of S_0 is similar in both systems.

The factor-of-three-higher mass of Re compared to Fe and, at the same time, a very similar Debye temperature mean that the instantaneous recoil of Fe as a result of the N_2 collision is significantly larger. This implies that less translational energy of N_2 is available to surmount the barrier. This explains the experimentally observed higher activity of Re at lower energies. Preliminary 3D simulations qualitatively agree with this observation. Similar conclusions were drawn for different masses in the gas phase (H_2 versus N_2) colliding with a copper surface [35].

The simulations presented here are based on a new form of PES compared to our previous study. On this PES, the potential energy at the bottom of the cross-

ing region (seam) between V_1 and V_2 relative to the gas phase is 59 kJ/mol (0.6 eV). This potential reflects better asymptotic physical characteristics with steeper repulsive walls. As a result the effective barrier is narrower at lower energies which seems better to reproduce the experimental data.

Billing et al. [11,12] have performed an extensive simulation of the N_2 /Re(0001) system. Their study includes a classical description of the molecular orientation, surface corrugation and surface motion. In addition, the two degrees of freedom addressed in this study were treated quantum mechanically. Their results, shown in fig. 4, have the same qualitative dependence of S_0 on E_n . The low-energy region is represented better than in our calculations mostly due to the convolution with the incident-beam energy distribution and averaging effect due to the extra degrees of freedom. From the figure, it is apparent that their value of the interaction potential, V_{12} , is too low. This results in their S_0 being one to two orders of magnitude too low compared with the experimental data presented here for energies above 0.3 eV.

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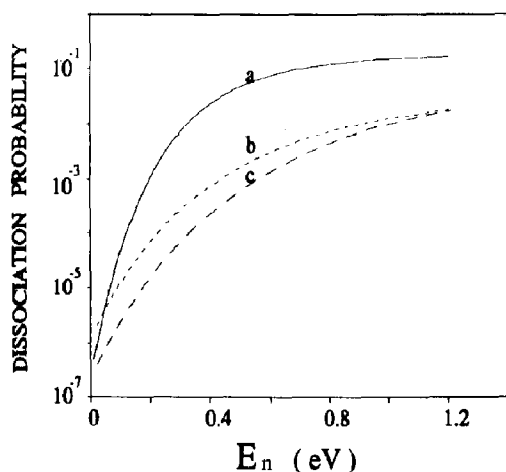


Fig. 4. Comparison of the dependence of S_0 on E_n . (a) Current simulation of N_2 on Re(0001). (b) The simulation of Billing et al. [11,12] for the same system. (c) The experimental results of N_2 on Fe(111) due to Rettner et al. [7].

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