N₂ dissociative adsorption on Ru(0001): The role of energy loss

L. Diekhöner,[a] H. Mortensen, A. Baurichter, E. Jensen, V. V. Petrunin, and A. C. Luntz

Fysisk Institut, Syddansk Universitet: Odense Universitet, Campusvej 55, 5230 Odense M, Denmark

New molecular beam experiments on the dissociation probability S_0 for N₂ on Ru(0001) are presented. These are in general agreement with prior measurements and exhibit very unusual behavior; a very slow increase of S_0 with incident kinetic energy E and the fact that S_0 is still only $\sim 10^{-3}$ at incident energies considerably above the barrier. A simple dynamical model is developed to describe this unusual sticking behavior. The key aspect is that there is considerable energy loss Δ from E upon initial impact with the surface (principally to the lattice) and only $E - \Delta$ is then available to surmount the activation barrier in the exit channel. Using experimentally measured values of Δ from scattering experiments gives good qualitative agreement of this model with the measured S_0. One implication of the strong energy loss is that there is an apparent violation of detailed balance when comparing only the reactive fluxes of activated adsorption and associative desorption. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1413746]

I. INTRODUCTION

The activated adsorption of N₂ on Ru(0001) has attracted much attention in the surface science community over recent years.[1] In large part this is due to the possible role of supported Ru as an end catalyst for commercial NH₃ synthesis, where the rate-limiting step in NH₃ synthesis on Ru is the dissociative adsorption of N₂. In well-defined surface science studies, Ru(0001) is often taken as a model for the catalyst and the dissociation is strongly activated on the bare surface. Theoretical estimates are of a barrier height of ca. 2 eV and lying principally along the N–N vibrational coordinate.[2–5] On the other hand, high pressure thermal rate studies of NH₃ formation from N₂ and H₂ on both Ru(0001)[6] and model catalysts[7] are only consistent with a much lower barrier to N₂ dissociation. This inconsistency has recently been resolved by the finding that the barrier for thermal N₂ dissociation is strongly lowered at steps and defects.[4] This conclusion is also consistent with the original 300 K thermal experiments which found a N₂ dissociation probability on Ru(0001) of $\leqslant 10^{-12}$.[8] Thus, the thermal catalytic process is dominated by steps and defects, while the higher barrier dissociation on the terraces is more relevant to consideration of theoretical surface dynamics. In this paper, we emphasize only dissociative adsorption on the terraces.

Recent measurements of associative desorption of N₂ from Ru(0001) find lower bounds to the adiabatic barrier to dissociation $V^*(0)$ on the terraces from the highest N₂ translational energies observed in the desorption.[5,9,10] These experiments find that the barrier is strongly dependent upon N coverage on the surface (Θ_N) and varies from $V^*(0) \approx 1.8$ eV at $\Theta_N \leqslant 0.25$ to $V^*(0) \geqslant 3$ eV at $\Theta_N \geqslant 0.7$. This increase of the dissociation barrier with Θ_N was previously inferred indirectly from peak shifts in N₂ thermal programmed desorption (TPD) with Θ_N (Refs. 9 and 11) and is

also in nearly quantitative agreement with density functional calculations (DFT) of the barrier.[5,10,12] The associative desorption experiments also demonstrate that considerable energy loss to the lattice must accompany desorption, although the nature of this energy loss is at this stage theoretically ill defined.[10]

At present, the "benchmark" for understanding the general process of activated adsorption is based on extensive molecular beam studies of adsorption dynamics, laser state resolved associative desorption experiments and theory for the system H₂/Cu(111) or Cu(100).[13–17] The general picture that has emerged is that a simple two-dimensional (2D) model gives a good approximate description of the translational and vibrationally resolved dissociation/association dynamics. However, inclusion of barrier corrugation, H₂ rotation or alignment requires higher dimensional PES and dynamics. Most important for the subject of this paper is the conclusion that the coupling to the lattice degrees of freedom seems quite weak and that a description of the dissociation dynamics assuming a rigid lattice is a good approximation. Of course, very small effects due to coupling to the lattice are observed experimentally, e.g., as a broadening of the sticking functions with surface temperature T_s.[15,18] In addition, the dissociative adsorption and the associative desorption for H₂/Cu(111) seem well related via detailed balance.[13] N₂ dissociation on Ru(0001) provides another prime example of activated adsorption, with a barrier far into the exit channel (along the vibrational coordinate). Certainly from the dynamical perspective, one issue is whether the general lessons learned from H₂/Cu(111) are applicable to N₂/Ru(0001) as well.

To our knowledge, the dissociative adsorption of N₂ on Ru(0001) has now been measured in three independent supersonic molecular beam experiments as well as thermally. In the first of these, Romm *et al.*[19] found that the N₂ dissociation probability on the bare surface (S_0) increased slowly with incident normal translational energy (E) over the range

0.15 to 4 eV. S_0 leveled off at ca. 10^{-6} at low E and at ca. 10^{-2} at high incident E [where $E \gg V^*(0)$], although the reproducibility of the low E results was later questioned by the same group of authors.[20] It has been argued that S_0 at low E is dominated by steps and defects.[4,21,22] Romm et al.[19] also found that S_0 increased nearly an order of magnitude when changing the nozzle temperature T_n from 700 K to 1800 K and this indicates some vibrational (v) activation of the dissociation as well as translational. Because of the small S_0 at high E, the authors suggested that a nonadiabatic tunneling mechanism was responsible for the dissociation. Romm et al.[20] also observed a large isotope effect in S_0 and cited this as further evidence for the nonadiabatic tunneling model. We note, however, that no isotope effect was observed in associative desorption experiments and this was taken as evidence against the importance of tunneling.[10] It has also recently been pointed out that this nonadiabatic tunneling model is in reality dominated by only apparent tunneling related to the high momentum tail of the initial vibrational state rather than true tunneling.[23] In later sticking experiments, over a small energy regime (0.98 eV–1.2 eV), Egeberg et al.[22] have clarified the role of defects in molecular beam sticking experiments by specifically poisoning step sites. They also observed a much stronger apparent dependence of S_0 with E and generally questioned the correctness of the experimental results of Romm et al.

In this paper, we present new molecular beam measurements of S_0 for N$_2$/Ru(0001) over an energy range of 1.4–3 eV and at a constant vibrational temperature of 1100 K. Our experimental results are in good qualitative agreement with those of Romm et al.,[19] especially the slow rise of S_0 with E and the fact that $S_0 \ll 1$ at $E > V^*(0)$. However, we do not agree with their assertion that this is caused by a nonadiabatic tunneling mechanism. Instead, we present a simple model that this is due to energy loss Δ from E upon impact with the surface, principally to the lattice (Δ_q). Energy that is lost from E to nonreactive coordinates is not then available to overcome the activation barrier. Combining simple 2D dynamics with the energy loss observed in state-resolved (TOF–REMPI) scattering experiments[24] gives good qualitative agreement with the measured S_0, including the leveling off of $S_0 \ll 1$ at $E > V^*(0)$. However, we also find that this model does not account for the relatively weak effect of vibrational excitation on S_0, so that energy loss from the vibrational coordinate as well as the translational coordinate is important in the dissociation dynamics. This is consistent with conclusions necessary to explain associative desorption experiments of N$_2$ from Ru(0001).[10] We also show that because of the large energy loss, both in activated adsorption and associative desorption, a comparison of purely reactive fluxes gives an apparent violation of detailed balance. In sum, the activated adsorption of N$_2$ on Ru(0001) is not at all similar to the H$_2$/Cu(111) "paradigm" of activated adsorption.

II. EXPERIMENT

All experiments were performed in a molecular beam-surface science machine described in detail previously.[11,25,26]

The Ru(0001) surface was of very high quality, with defect densities of only 0.25%. Cleaning procedures for this sample and its characterization are described elsewhere.[11] Sticking measurements were made in the conventional way of exposing a clean Ru(0001) surface to high energy seeded supersonic molecular beams of N$_2$ at normal incidence with energy E and nozzle temperature T_n and measuring the buildup of N on the surface as a function of exposure. To minimize problems of contamination in measuring small sticking coefficients, high quality gases were used throughout; N$_2$ (99.9999% purity) in H$_2$(99.9997%) or He (99.9999%).

The kinetic energies of the supersonic beams at $T_n \approx 1100$ K were varied by varying the composition of the seed mixture and were measured accurately by their time-of-flight (TOF). In all cases the energy distributions were described by a spread $\Delta E / \bar{E} \le 0.15$, where $\bar{E}$ is the average and ΔE the FWHM of the energy distribution. For beams of N$_2$ seeded in H$_2$, an alumina (Al$_2$O$_3$) ceramic nozzle was used to avoid any catalytic chemistry occurring in the nozzle. Since it was not possible to attach a thermocouple to the alumina nozzle, the nozzle temperature (T_n) was determined indirectly by measuring the TOF curve of a pure He beam under the same heating conditions as used for the sticking experiments and extracting T_n from the velocity distribution. Agreement between T_n inferred indirectly in this way and the actual T_n was verified using a stainless steel nozzle where T_n could be measured. Nevertheless, because of the indirect means of measuring T_n, we assume an uncertainty in the absolute value of T_n of ca. 100 K. E was varied only by changing the mixing ratio of N$_2$ and H$_2$ with the heating current to the nozzle (and hence T_n) kept constant at $T_n = 1100$ K. A single experiment at $T_n = 1150$ K was also made with N$_2$ seeded in He in a stainless steel nozzle in which T_n was measured accurately using a thermocouple. This allows a check of both the indirect measurement of T_n using the velocity distribution and whether any artifacts occurred in the sticking measurements due to seeding in H$_2$.

Relative N$_2$ fluxes at the Ru(0001) surface for the various energy beams was determined by a stagnation volume method, i.e., measuring the N$_2$ partial pressure build up in the chamber with a nonline-of-sight quadrupole mass spectrometer (QMS) when the beam hit an inert quartz flag. To convert these relative fluxes to absolute fluxes, we need the area of the beam on the surface, the absolute sensitivity of the QMS and the pumping speed of the vacuum system. All were measured, but this introduces an estimated uncertainty of a factor of 5 in the absolute calibration of S_0 values, although the relative values are much better determined.

Relative N coverage on Ru(0001) as a function of beam exposure was measured by integrating the N$_2$ temperature programmed desorption (TPD) into a differentially pumped QMS, with an orifice of 5 mm in diameter placed ca. 2 mm from the surface.

Mass 14 was generally used for detection to avoid any complications due to CO desorption. Absolute normalization of the coverage Θ_N was obtained by comparing the N$_2$ TPD signal at mass 28 to a CO TPD at saturation at 300 K($\Theta_{CO} = 0.56$).[8] A plot of Θ_N versus exposure showed a nominal second order buildup of N on the surface. All values
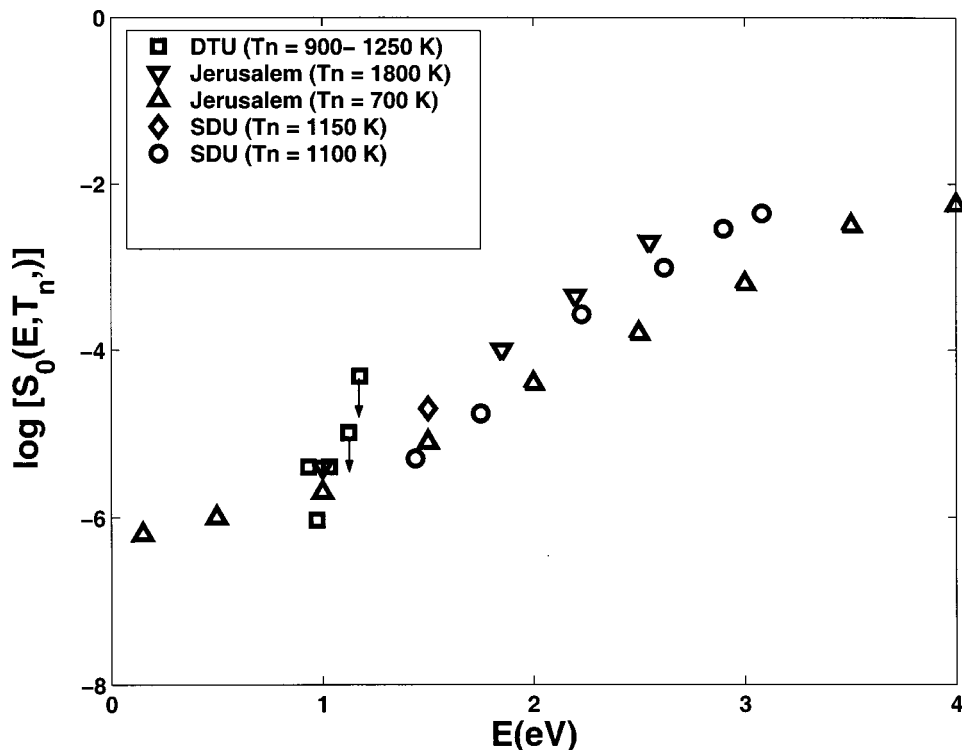
FIG. 1. Molecular beam measurements of N_2 dissociation on Ru(0001) plotted as $\log[S_0(E,T_n)]$ vs normal translational energy E. Points labeled Jerusalem are from Ref. 19, those labeled DTU are from Ref. 22 and those labeled SDU are from this work.

of S_0 reported here were measured in the initial linear region of the uptake curve, i.e., at coverage $\Theta_N \sim 0.02$ ML. All dose times were <1.5 h at $T_s = 575$ K. No contamination of the sample after dosing with the beam was observable with either TPD or Auger. Nor was there any apparent problem with background N_2 dissociative adsorption reported by Egeberg *et al.*[22] Since this problem is presumably due to adsorption at steps/defects, we may have avoided this by using a Ru(0001) surface with a very low defect density (0.25%) and by measuring S_0 when Θ_N was an order of magnitude larger than this defect density.

III. RESULTS AND DISCUSSION

Figure 1 compares all three beam measurements of S_0. Our results agree qualitatively with those of Romm *et al.*[19] over the common energy range. Both our results and most of those of Romm *et al.* were done with approximately a constant nozzle or vibrational temperature T_n. The experiments of Egeberg *et al.*[22] show a much higher apparent dependence on E, although in fact these points were obtained by varying E principally by varying T_n. We believe that most of their apparent difference in the E dependence is due to the fact that their experiments do not fully separate the translational activation from the vibrational activation.

There are three striking qualitative features to the sticking data in Fig. 1. First, the approximately constant $S_0 \approx 10^{-6}$ at low incident E is atypical. It has been argued by Egeberg *et al.* that this limit is set by low barrier dissociation at steps/defects on the surface and that dissociation on terraces should be much lower at low E. As evidence, Egeberg *et al.* show that dissociation at $E=1.1$ and 1.2 eV in their experiments is decreased nearly a factor of 2 when a small amount of Au is adsorbed on the surface and blocks the steps

(indicated by the downward arrows in Fig. 1). Although they use this evidence to argue that steps are not important under molecular beam conditions, we believe that this shows that at least half of the dissociation at these energies is still governed by steps. Presumably at lower E, steps/defects totally dominate the sticking behavior and at higher E, the dissociation at terraces dominates S_0.

The second striking feature of the sticking data of Fig. 1 is the relatively weak dependence on T_n relative to other activated adsorption systems which show vibrational activation, i.e., $H_2/Cu(111)$[14,27] and $CH_4/Ni(100)$[28] or Ru(0001).[29] This is particularly surprising since the 2D PES obtained in DFT calculations[3] to describe dissociation is an extreme case of an exit channel barrier (see Fig. 2). In this case, it is anticipated that vibrational activation should be very strong. Anticipated 2D (stiff lattice) dissociation dynamics $S_{2D}(E,v)$ based on this PES are shown in Fig. 3 as the dashed lines. These were simply constructed as traditional "S" shaped vibrationally resolved sticking functions for $V^*(0)=1.8$ eV and vibrational efficacy $\eta_v = 1$.

The third and most striking aspect in the results of Fig. 1 is the very slow increase of S_0 with E and that $S_0 \approx 10^{-3}$ at 3 eV, i.e., $S_0 \ll 1$ at $E \gg V^*(0)$. This is most definitely atypical as most activated adsorption systems, e.g., $H_2/Cu(111)$[14,27] or $CH_4/Ni(100)$,[28] approach $S_0 \approx 1$ at $E \gg V^*(0)$. It is this fact that led Romm *et al.*[19] to propose a nonadiabatic tunneling mechanism. A similar behavior has been observed and explained similarly by them for N_2 dissociation on Re as well.[30,31] Note that the dissociation behavior for 2D dynamics (Fig. 3) rapidly increases to unity S_0 once $E > V^*(0)$. This means that the fact that $S_0 \ll 1$ cannot be rationalized simply in terms of 2D dynamics, even for such a strong exit channel barrier as in Fig. 2. We anticipate that
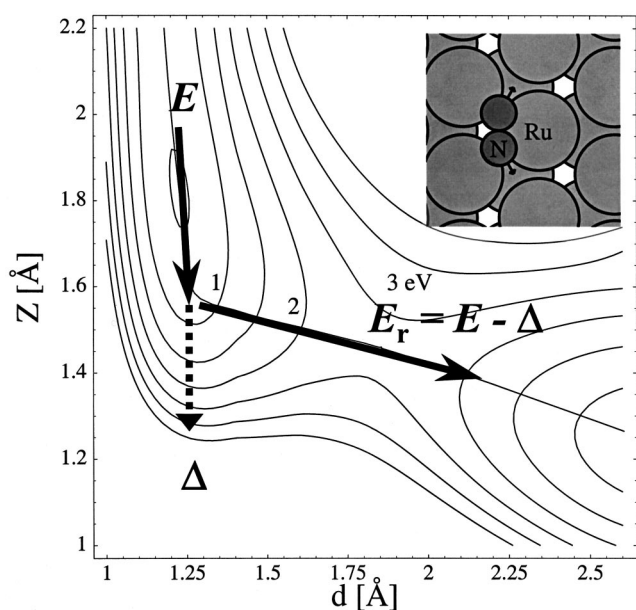
FIG. 2. Equipotential contours for N$_2$ dissociation on Ru(0001) from DFT calculation (Ref. 3). Z is the distance of N$_2$ from the surface and d is the N–N bond length. Arrows schematically show that if a N$_2$ molecule incident with normal translational energy E loses energy Δ (principally to the lattice) in the entrance channel, then only energy $E_r = E - \Delta$ is available to overcome the barrier to dissociation in the exit channel.

generalization of the dynamics to all 6 molecular coordinates will not materially change the inability of conventional adiabatic stiff lattice dynamics to rationalize that $S_0 \ll 1$ at $E \gg V^*(0)$.

In general, it is possible to estimate adiabatic barriers to activated adsorption from the "threshold" of the $v = 0$ sticking curve.[32] However, because of the unconventional behavior of S_0 observed for N$_2$/Ru(0001), we do not see any way to extract an estimate of a barrier to dissociation directly from the experimental sticking results. Romm *et al.* quoted a

barrier as 2.2 eV (latter changed to 1.8 eV) based upon a fit of their nonadiabatic theoretical model to the experiments. However, since we do not believe that nonadiabatic tunneling is important in the sticking, we find this estimate and connection to the observed S_0 rather tenuous. We do note, however, that the adiabatic barrier $V^*(0) \approx 1.8$ eV obtained from associative desorption experiments at low Θ_N (Ref. 10) is in very good agreement with the barrier calculated in DFT calculations,[3,5] and hence do take this as the adiabatic barrier appropriate to describe the sticking experiments.

Since N$_2$ does not dissociate appreciably at high incident energy, it must predominately scatter back into the gas phase. In order to understand which other coordinates are most important for describing the dissociation dynamics, we have performed a rather complete series of REMPI-ion TOF inelastic scattering experiments. For an incident N$_2$ in internal vibrational, rotational quantum state v,J and a given incident energy E, these experiments measure the full state distribution; v_f, J_f and average final normal translational energy $\langle E_f \rangle$ of the v_f, J_f state produced in scattering from the surface. These experiments will be reported in detail elsewhere.[24] Here, we simply summarize a result at high incident energy. At $E = 2.7$ eV, vibrational excitation and de-excitation is minimal and not measurable ($\Delta\varepsilon_v \approx 0$), rotational excitation is modest $\Delta\varepsilon_R = 0.18$ eV but the average normal energy loss for the incident v,J state is enormous, $\langle \Delta \rangle = E - \langle E_f \rangle = 1.5$ eV! $\langle \Delta \rangle$ is principally due to energy loss to the lattice $\langle \Delta_q \rangle$, with $\leq 15\%$ due to conversion of E to a component of energy parallel to the surface $E_\parallel$. Energy is transferred from the principal reactive coordinates (E, v) into largely nonreactive coordinates ($\Delta_q, E_\parallel$). The fraction of incident energy lost $\langle \Delta \rangle / E$ shows that this varies from ca. 0.1 at $E = 0.2$ eV to over 0.55 at $E = 2.5$ eV. The magnitudes and E dependence are generally consistent with the energy transfer of rare gasses to lattices.[33] The key finding in the scattering experiments is that the dominant energy loss mode from
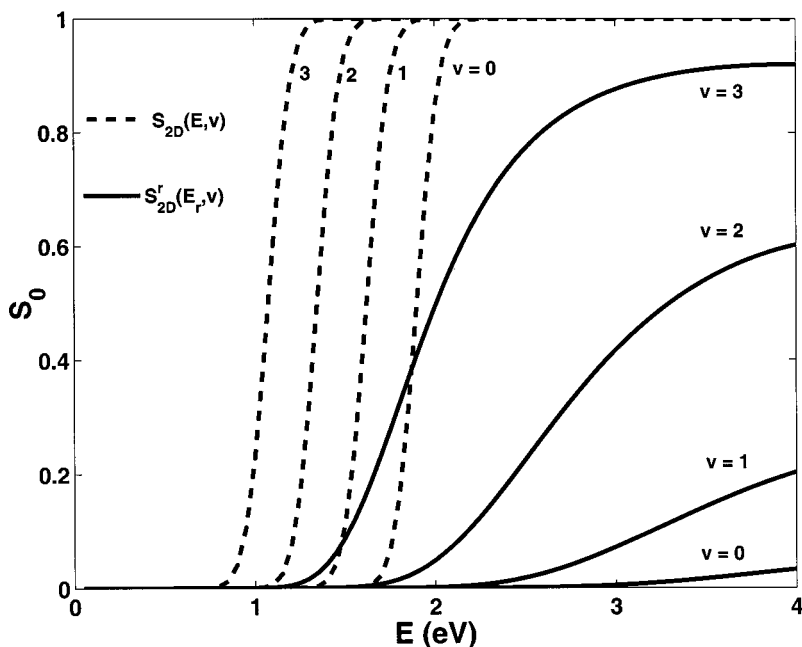
FIG. 3. Anticipated vibrationally (v) resolved dissociation probabilities S_0 as a function of normal translational energy E for N$_2$ dissociation on Ru(0001). Dashed lines assume 2D stiff lattice dynamics $S_{2D}(E,v)$ on the PES of Fig. 2 and the solid lines are for the energy loss model $S_{2D}^r(E_r, v)$ outlined by the arrows in Fig. 2 and discussed in the text.
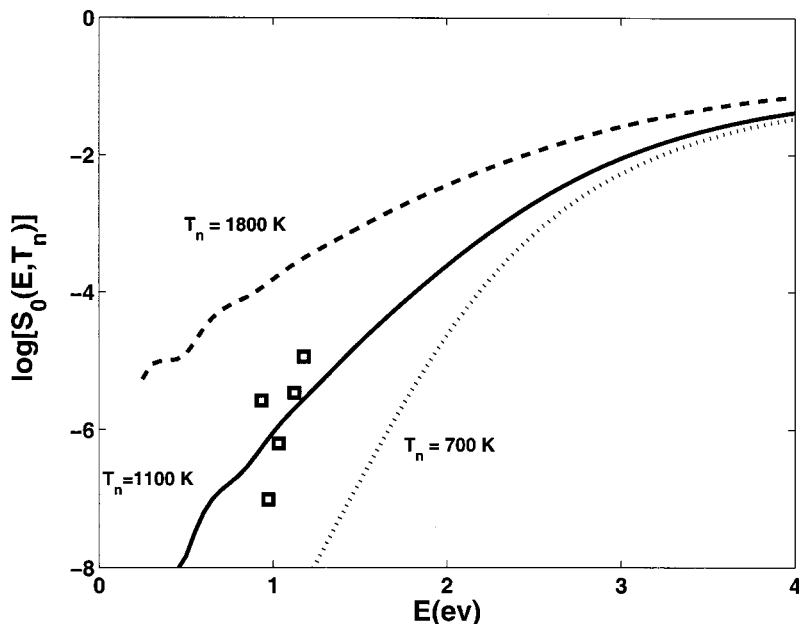
FIG. 4. Predicted dissociation probabilities S_0 of N_2 on Ru(0001) as a function of nozzle (vibrational) temperature as noted on the figure and normal translational energy E derived from the energy loss model (solid lines of Fig. 3). The square points are predictions of the model for the experimental conditions of Ref. 22. All predictions should be compared with the experimental results of Fig. 1.

E is to the lattice and that this loss is in fact very large at the energies required to surmount the barrier.

A simple model that couples energy loss from E to the lattice with dissociation has previously been proposed by Hand and Harris,[34] so-called "dynamic recoil." This has been discussed in detail with respect to CH_4 dissociation on transition metals.[35] However, this model is really only appropriate for an entrance channel barrier and hence of very dubious validity for N_2/Ru(0001). Instead, we propose that the role of lattice coupling (and coupling to $E_\parallel$) for an exit channel barrier is better described as outlined schematically in Fig. 2. In this case, energy Δ is lost from E upon impact with the surface in the entrance channel. Since energy in the lattice (and probably also $E_\parallel$) is not reactive, only $E_r = E - \Delta$ is then available to surmount the barrier in the exit channel. A very simple model of this gives

$$S_0(E,v) \approx S_{2D}^r(E_r,v) = \int S_{2D}(E-\Delta,v)P(\Delta)d(\Delta),$$

where $S_{2D}^r(E_r,v)$ is the 2D dissociation functional for translational energy distribution E_r and vibrational state v. $P(\Delta)$ is the distribution of energy loss Δ for impact at initial energy E.

Although we do not know in detail $P(\Delta)$ for molecules that ultimately dissociate, we assume that this distribution is the same as for those that scatter inelastically from the surface. This means that the energy loss distribution for impact parameters (and orientations) that ultimately lead to dissociation are roughly the same as those averaged over the entire surface in the scattering experiments. We take the form of $P(\Delta)$ as Gaussian, i.e., as predicted in forced oscillator models of gas-surface energy transfer,[36]

$$P(\Delta) \propto \exp[-(\Delta - \langle\Delta\rangle)^2/\sigma^2],$$

with $\sigma = \sqrt{\langle\Delta\rangle\varepsilon_q}$ and $\varepsilon_q = 20$ meV, a typical phonon frequency. Note that both Δ and σ are strong implicit functions of E. This form of $P(\Delta)$ is consistent with the fact that energy loss to the lattice dominates Δ. If we take $\langle\Delta(E)\rangle$ as

measured in the scattering experiments, then this model predicts the sticking labeled $S_{2D}^r(E_r,v)$ in Fig. 3.

$S_{2D}^r(E_r,v)$ is vastly different than $S_{2D}(E,v)$, especially for the lowest v states which dominate sticking experiments. The E center for the "S" shaped $S_{2D}^r(E_r,v)$ is at much higher translational energies than $S_{2D}(E,v)$ and the apparent amplitudes are much smaller. The qualitative rational for the observed behavior is that the low v states lose so much energy from the reactive coordinate E before reaching the transition state that they have a hard time dissociating. Since both $\langle\Delta\rangle$ and σ increase with energy, the net effect is a shifted and slowly rising $S_{2D}^r(E_r,v)$ with E, with the largest effects for low v (high E). The exact shape and magnitude of $S_{2D}^r(E_r,v)$ depends more on the detailed properties of the energy loss $P(\Delta)$ (which is of course only approximately known) than on the stiff lattice dynamics $S_{2D}(E,v)$ (or generalizations to higher dimensional stiff lattice dynamics). Thus, we do not believe that sticking experiments on these high exit channel barrier system are very revealing of the underlying stiff or relaxed lattice PES as obtained in DFT theory. Rather, the sticking seems to be much more determined by details of energy loss on impact with the surface. We believe this is the reason that it is virtually impossible to make a realistic barrier estimate directly from the observed sticking behavior.

Averaging $S_{2D}^r(E_r,v)$ over the principal nozzle (vibrational) temperatures T_n used in the experiments gives the model "predictions" of the experimental sticking in Fig. 1. This is shown in Fig. 4. Many of the striking qualitative features of Fig. 1 are reproduced in this simple model. The generally slow increase in sticking with incident energy at constant T_n is predicted by the model, and most importantly that sticking is limited at high E, i.e., that $S_0 \ll 1$ at $E > V^*(0)$ is reproduced in the model. Thus, we do not believe it is necessary to invoke a nonadiabatic tunneling mechanism to rationalize this behavior. It is a simple consequence of the
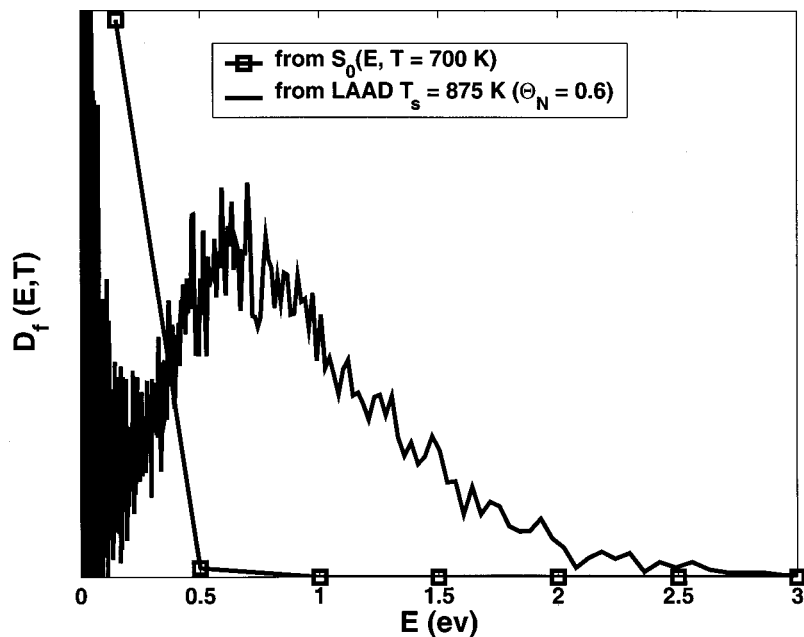
FIG. 5. Comparison of the energy E resolved desorption flux at temperature T, $D_f(E,T)$, obtained experimentally from laser assisted associative desorption (LAAD) experiments (Ref. 10) and that predicted from detailed balance and measurements of dissociative sticking $S_0(E,T)$. $D_f(E,T)$ for $E<0.2$ eV from LAAD is dominated by noise related to establishing the experimental background "zero signal."

measured large energy loss from E to nonreactive coordinates at high E. In addition, since the energy loss Δ depends on the mass of the incoming particle, we anticipate a significant isotope effect in $S_{2D}^r(E_r,v)$ and hence in the model for sticking. While this energy loss model does predict an isotope effect of the same magnitude in $S_0(E,T_n)$ as that observed experimentally in sticking,[20] the energy dependence of the predicted and observed isotope effects is not identical, i.e., the predicted isotope effect does not disappear at high E. Nevertheless, the qualitative fact is that a significant "heavy atom" isotope effect is predicted by the energy loss model and therefore a tunneling mechanism is not required to rationalize this behavior.

This model also predicts that simultaneous variation of both E and T_n (points in Fig. 4) will produce a much larger apparent dependence on E. We believe this rationalizes the apparent disagreement of the results of Egeberg *et al.* compared to those of Romm *et al.* and the new results reported here. This model does not reproduce two of the qualitative features of the experimental results in Fig. 1, however. The model predicts that S_0 continues to decrease at lower and lower E instead of leveling off at $S_0 \approx 10^{-6}$ at low E. We take this as further evidence that steps/defects dominate the experiments at low E as these are not present in the model. It is also apparent that the model still grossly over estimates the role of T_n in activating dissociation. We believe that this implies that energy transfer from the vibrational coordinate to the lattice, as well as from the translational coordinate, is important in the dissociation dynamics. Exactly the same conclusion was reached in analyzing the energy resolved associative desorption flux of N$_2$ from Ru(0001).[10] The nature of this vibrational energy loss is not at all clear so we have not tried to incorporate it in a more general model.

It has proven helpful in discussions of H$_2$/Cu(111) (and other) activated dissociation dynamics to relate the state resolved dissociative adsorption flux to that from associative desorption experiments via detailed balance.[13,14] This is tra-

ditionally done by assuming that detailed balance is valid in relating solely the reactive fluxes.[37] Under isothermal conditions, $T_n = T_s \equiv T$, the expression of detailed balance in terms of the reactive fluxes normal to the surface is given as $D_f(E,T) \propto E \exp(-E/k_BT)S_0(E,T_n=T,T_s=T)$, where $D_f(E,T)$ is the associative desorption flux at normal translational energy E at surface temperature $T_s \equiv T$ and S_0 is the dissociation probability for the given conditions. This form is equivalent to the usual state resolved formulation and merely takes the Boltzmann weighted sum over the internal states for each.

Figure 5 shows a comparison of $D_f(E,T)$ obtained experimentally in associative desorption experiments[10] with that predicted from the above equation. Although the experimental conditions (e.g., Θ_N) are not equivalent in the adsorption and associative desorption experiments, it is clear that the qualitative behavior is not at all the same and this implies that application of detailed balance to relate these two experiments is not valid. Both Egeberg *et al.*[22] and we have argued that the sticking at low E is dominated by steps/defects and this is what causes the detailed balance predicted peak in $D_f(E,T)$ at low E. On the other hand, many arguments have been presented elsewhere[10] that these associative desorption experiments probe desorption from terraces rather than steps. Thus, the two experiments probe a different phase space so that detailed balance is not anticipated to be a good approximation in relating the two.

It was also observed previously that in the associative desorption experiments, the dependence on E in $D_f(E,T)$ was completely independent of T.[10] Since the experimental S_0 is also independent of T_s and only weakly dependent on T_n, $D_f(E,T)$ predicted by detailed balance should be approximately $\propto \exp(-E/k_BT)$, i.e., exponential with $1/T$. This outlines a more fundamental problem in using only the reactive fluxes for detailed balance when there is large energy loss. This is outlined pictorially in Fig. 6. Figure 6(a) gives a representation of activated sticking as described by the

Adsorption   (a)

E

N_2

$E_r = E - \Delta_q (a)$ N---N   N   N

$\Delta_q(a)$

Detailed balance   (b)

$E = E_r + \Delta_q (a)$

N_2

E_r N---N   N   N

$\Delta_q(a)$

Desorption   (c)

$E = E_r - \Delta_q (d)$

N_2
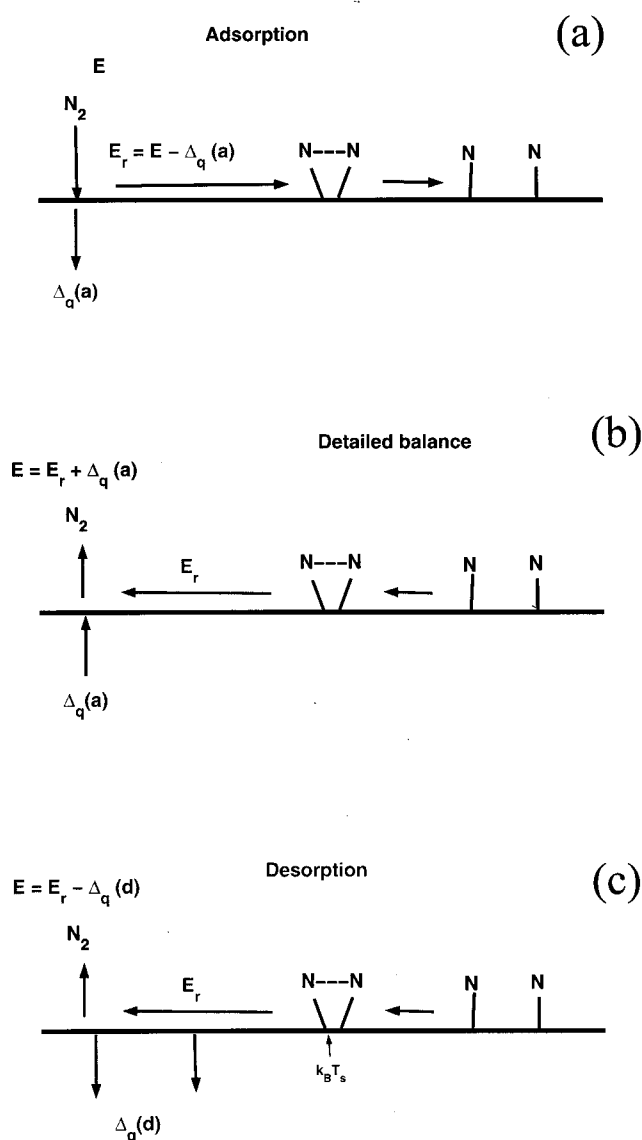
E_r N---N   N   N

$k_B T_s$

$\Delta_q(d)$

FIG. 6. Schematic representation of proposed models that include significant energy loss for dissociative adsorption (a), the corresponding desorption process necessary to fulfill detailed balance (b), and the actual proposed model of associative desorption (Ref. 10) (c). For purposes of the figure, we simply assume that all energy loss Δ is to the lattice, i.e., that $\Delta(a) = \Delta_q(a)$ and $\Delta(d) = \Delta_q(d)$.

model developed here. It is dominated by large energy loss $\Delta(a)$, principally to the lattice. Detailed balance is based on reciprocity. If we assume that the only important component of a detailed balance comparison is the reactive flux, then detailed balance would require the process described by Fig. 6(b). While this process certainly could occur, it must have a low probability since it requires the annihilation of spontaneously created multiple phonons of high energy. Figure 6(c) shows the view of associative desorption for $N_2/Ru(0001)$ developed in Ref. 10. It is dominated by energy loss, principally to the lattice, $\Delta(d)$ and this process is not at all equivalent to the phase space required for the detailed balance comparison using solely reactive fluxes.

If $\Delta(a)$ and $\Delta(d)$ are negligible compared to other characteristic energies [E and $V^*(0)$], then an expression of detailed balance comparing solely the reactive fluxes is likely

to be a good approximation. This is the case for the comparisons of $H_2/Cu(111)$.[13,14] However, when $\Delta(a)$ and $\Delta(d)$ are large, as is the case for $N_2/Ru(0001)$, then the application of detailed balance must include nonreactive (inelastic) as well as the reactive fluxes. This issue of the role of energy loss in sticking and detailed balance has been discussed previously in terms of "dynamic recoil"[16,38] but to our knowledge this is the first experimental verification of the problems it causes.

IV. SUMMARY AND CONCLUSIONS

There has been considerable controversy over the initial sticking coefficients for N_2 on Ru(0001), in part because the behavior with incident energy E is very strange. This paper presents additional molecular beam measurements of S_0 as a function of E at constant T_n. We are in qualitative accord with the prior measurements and validate the claim that $S_0 \ll 1$ at $E > V^*(0)$. However, instead of invoking a nonadiabatic tunneling mechanism to rationalize this behavior, we believe this is simply the natural consequence of strong energy loss Δ from E on impact with the surface, principally to the lattice. A simple dynamical model based on energy loss and then sequential dissociation, where the energy available for reaction is $E_r = E - \Delta$, gives reasonable qualitative accord with the experimental results, especially the fact that S_0 increases only slowly with incident energy and that $S_0 \ll 1$ at energies where $E \gg V^*(0)$. This model also qualitatively rationalizes a significant "heavy atom" isotope effect in the sticking. However, there is also only a moderate dependence on T_n or vibrational activation in the experimental sticking. Not only is this inconsistent with 2D dynamics on the PES obtained in DFT calculations, but it is not accounted for by the simple model with energy loss from E either. We speculate that there is an additional energy loss mechanism from the vibrational coordinate as well. This is in accord with dynamics inferred previously for associative desorption.[10]

A direct comparison of the sticking results with prior associative desorption experiments does not exhibit detailed balance. In part this is due to the fact that the sticking experiments are dominated by steps/defects at low E, while the associative desorption experiments probed recombination on the terraces. In addition, we argue that when strong lattice losses occur in adsorption/desorption, a comparison of detailed balance cannot be made using solely the reactive fluxes. Inelastic fluxes must also be included.

[1] K. Jacobi, Phys. Status Solidi A **177**, 37 (2000).
[2] J. J. Mortensen, Y. Morikawa, B. Hammer, and J. K. Nørskov, J. Catal. **169**, 85 (1997).
[3] M. J. Murphy, J. F. Skelly, A. Hodgson, and B. Hammer, J. Chem. Phys. **110**, 6954 (1999).

[4] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).

[5] L. Diekhöner, H. Mortensen, A. Baurichter, A. C. Luntz, and B. Hammer, Phys. Rev. Lett. **84**, 4906 (2000).

[6] S. Dahl, P. A. Taylor, E. Törnqvist, and I. Chorkendorff, J. Catal. **178**, 679 (1998).

[7] R. Schlögl, in *Catalytic Ammonia Synthesis*, edited by J. R. Jennings (Plenum, New York, 1991), p. 19.

[8] H. Dietrich, P. Geng, K. Jacobi, and G. Ertl, J. Chem. Phys. **104**, 375 (1996).

[9] L. Diekhöner, H. Mortensen, A. Baurichter, and A. C. Luntz, J. Vac. Sci. Technol. A **18**, 1509 (2000).

[10] L. Diekhöner, H. Mortensen, A. Baurichter, and A. C. Luntz, J. Chem. Phys. **115**, 3356 (2001).

[11] L. Diekhöner, A. Baurichter, H. Mortensen, and A. C. Luntz, J. Chem. Phys. **112**, 2507 (2000).

[12] B. Hammer, Phys. Rev. B **63**, 205423 (2001).

[13] H. A. Michelsen, C. T. Rettner, and D. J. Auerbach, Springer Ser. Surf. Sci. **34**, 185 (1994).

[14] C. T. Rettner, H. A. Michelsen, and D. J. Auerbach, J. Chem. Phys. **102**, 4625 (1995).

[15] M. J. Murphy and A. Hodgson, J. Chem. Phys. **108**, 4199 (1998).

[16] G. R. Darling and S. Holloway, Rep. Prog. Phys. **58**, 1595 (1995).

[17] G.-J. Kroes, Prog. Surf. Sci. **60**, 1 (1999).

[18] H. A. Michelsen, C. T. Rettner, and D. J. Auerbach, Surf. Sci. **272**, 65 (1992).

[19] L. Romm, G. Katz, R. Kosloff, and M. Asscher, J. Phys. Chem. B **101**, 2213 (1997).

[20] L. Romm, O. Citri, R. Kosloff, and M. Asscher, J. Chem. Phys. **112**, 8221 (2000).

[21] S. Dahl, E. Törnqvist, and I. Chorkendorff, J. Catal. **192**, 381 (2000).

[22] R. C. Egeberg, J. H. Larsen, and I. Chorkendorff, Phys. Chem. Chem. Phys. **3**, 2007 (2001).

[23] N. E. Henriksen, F. Y. Hansen, and G. D. Billing, Chem. Phys. Lett. **330**, 139 (2000).

[24] H. Mortensen, E. Jensen, A. Baurichter, L. Diekhöner, V. V. Petrunin, and A. C. Luntz (unpublished).

[25] A. C. Luntz, M. D. Williams, and D. S. Bethune, J. Chem. Phys. **89**, 4381 (1988).

[26] H. Mortensen, L. Diekhöner, A. Baurichter, E. Jensen, and A. C. Luntz, J. Chem. Phys. **113**, 6882 (2000).

[27] C. T. Rettner, D. J. Auerbach, and H. A. Michelsen, Phys. Rev. Lett. **68**, 1164 (1992).

[28] P. M. Holmblad, J. Wambach, and I. Chorkendorff, J. Chem. Phys. **102**, 8255 (1995).

[29] J. H. Larsen, P. M. Holmblad, and I. Chorkendorff, J. Chem. Phys. **110**, 2637 (1999).

[30] M. Asscher, G. Haase, and R. Kosloff, Vacuum **41**, 269 (1990).

[31] M. Asscher, O. M. Becker, G. Haase, and R. Kosloff, Surf. Sci. **206**, L880 (1988).

[32] A. C. Luntz, J. Chem. Phys. **113**, 6901 (2000).

[33] H. F. Winters, H. Coufal, C. T. Rettner, and D. S. Bethune, Phys. Rev. B **41**, 6240 (1990).

[34] M. Hand and J. Harris, J. Chem. Phys. **92**, 7610 (1990).

[35] A. C. Luntz and J. Harris, Surf. Sci. **258**, 397 (1991).

[36] J. Harris, Phys. Scr. **36**, 156 (1987).

[37] M. J. Cardillo, M. Balooch, and R. E. Stickney, Surf. Sci. **50**, 263 (1975).

[38] J. Harris, Faraday Discuss. **96**, 1 (1993).