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Sticking coefficient for dissociative adsorption of N$_2$ on Ru single-crystal surfaces

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The dissociative chemisorption of N$_2$ on Ru(0001), Ru(10$\bar{1}$0), and Ru(11$\bar{2}$1) surfaces at 300 K was studied by means of high-resolution electron energy loss spectroscopy and thermal desorption spectroscopy. The initial sticking coefficient was determined to $s_0 = (1 \pm 0.8) \times 10^{-12}$, within the limits of error independent of surface orientation. On Ru(10$\bar{1}$0) and Ru(11$\bar{2}$1) small amounts of N can be dissolved into the subsurface region. © *1996 American Institute of Physics.* [S0021-9606(96)02301-2]

I. INTRODUCTION

The Haber–Bosch process for NH$_3$ synthesis on the Fe-based catalyst is well understood even in its atomic steps, and it is known that the dissociative adsorption of N$_2$ is rate limiting.[1–3] The following initial sticking coefficients for dissociative adsorption of N$_2$ on Fe surfaces were found: 7×10^{-8} [Fe(111)], 2×10^{-7} [Fe(100)], and 4×10^{-6} [Fe(111)].[4,5] Maximum sticking coefficients of about 4×10^{-5} were obtained by optimizing the surface potassium concentration for Fe(111) and (100) surfaces.[6] The reaction mechanism for the Ru-based catalyst[7–11] is not established yet, and it is our aim to contribute to the better understanding of the processes involved. Among them the dissociative adsorption of N$_2$ is certainly the most important one. For the Ru-based catalyst Cs is used as a promoter. Its influence on the sticking coefficient will be investigated in future work.

N atoms chemisorbed on Ru single-crystal surfaces have thus far been prepared by electron bombardment,[12,13] plasma discharge of N$_2$,[14] or dissociative adsorption of NH$_3$,[12,15,16] NO,[17–19] N$_2$H$_4$, or NH$_2$CHO.[20,21] Matsushima[13] noted that the sticking coefficient for dissociative adsorption of N$_2$ on Ru(0001) is smaller than 10^{-8} but did not give further details of his estimate. In our recent contribution[22] we quoted a value of 2×10^{-6} for this latter process independent of substrate temperature which was varied between 420 and 700 K. We discovered later that the hot filament of the ionization gauge increases the probability for dissociative chemisorption, probably by generation of a small fraction of long-lived vibrationally excited molecules.

Here we report on measurements, performed at 300 K, and show that, with the ionization gauge shut off, the initial sticking coefficient s_0 for thermal ground-state molecules is as low as 1×10^{-12}. We give experimental evidence that the surface stays clean enough during exposition of those high doses necessary to determine such a small sticking coefficient. We further show that this value is about the same for Ru(0001) and the more open Ru(10$\bar{1}$0) and Ru(11$\bar{2}$1) surfaces and hence is independent of surface crystallography.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum (UHV) apparatus with a base pressure of 1×10^{-11} mbar which was achieved by a pumping line completely free of oil consisting of a Ti sublimation pump (TSP), a turbomolecular pump with magnetic bearing (Leybold, NT 340M), a drag pump (Balzers, TCP015), and a diaphragm pump. The apparatus consisted of two chambers separated by a valve as described previously.[23] The upper chamber contained an argon gun, a quadrupole mass spectrometer, and a low-energy electron diffraction (LEED) optics; the lower chamber housed a high-resolution electron energy loss (HREEL) spectrometer, a so-called penultimate IBACH type which was found capable of a 1 meV energy resolution.[24,25] The lower chamber was kept at a pressure of 3×10^{-11} mbar when the upper chamber was filled by N$_2$ up to a pressure of several mbar during N$_2$ dosing. The HREEL spectra were taken in specular geometry at an emission angle of 60° with respect to the surface normal. The impact energy was 2.5 eV and the energy resolution was set to about 3–4 meV. The mass spectrometer, computer controlled with the LABVIEW program for quasisimultaneous measuring and positioned in the upper chamber, was used to perform TDS experiments with a heating rate of 3 K s^{-1}. For this purpose the sample was positioned in front of a short stainless-steel tube with a diameter of about the sample size so that the ionizer of the mass spectrometer accepted molecules only after desorption from the sample surface. To distinguish between CO and N$_2$ desorption, the mass spectrometer signals were recorded quasisimultaneously for e/m ratios of 14 and 28. The signal for $e/m = 2$ was recorded in order to check for H$_2$ desorption.

The Ru(0001) sample was mounted using W wires in narrow slits at the edges of the sample. The W wires were heated resistively. The two other—Ru(10$\bar{1}$0) and Ru(11$\bar{2}$1)— samples, were clamped between W wires and heated by electron bombardment from the backside. The crystal temperature was measured using a Ni–Cr/Ni thermocouple spot welded to the backside [Ru(0001)] or the upper edge sides [Ru(10$\bar{1}$0),Ru(11$\bar{2}$1)] of the samples. Cleaning of the surfaces was achieved by cycles of sputtering and annealing to 1560 K. The cleanliness was verified by LEED and HREELS. The purity of N$_2$ was 99.9999 vol % (Messer, Ger-

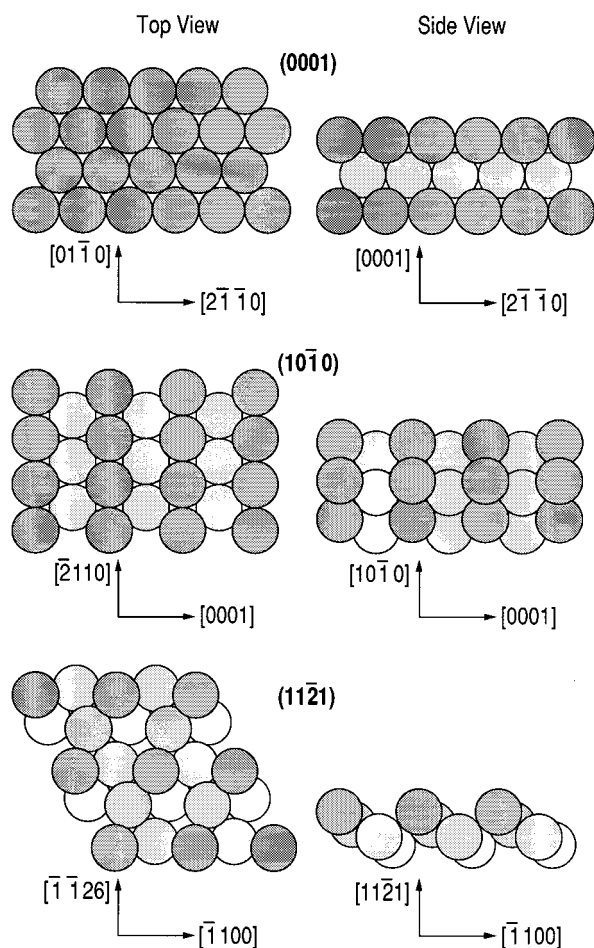---

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FIG. 1. Top and side view of different bulk-truncated Ru surfaces. Dark atoms are in the top layer, lighter atoms are in the layers below.
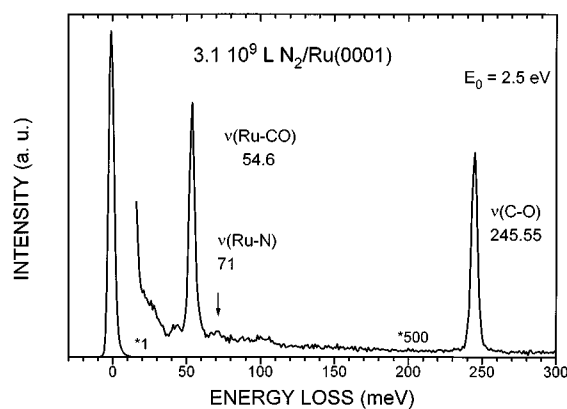

FIG. 2. HREEL spectrum for a Ru(0001) surface exposed to 3.1×10^9 L N$_2$ at 300 K. The spectrum was recorded in specular geometry with an angle of incidence of 60° with respect to the surface normal. Primary energy E_0 and vibrational modes ν are indicated.

many) with O$_2 \leqslant 0.5$ vpm, H$_2$O$\leqslant 0.5$ vpm, C$_x$H$_y \leqslant 0.1$ vpm, CO and CO$_2 \leqslant 0.1$ vpm, and Ar$\leqslant 1.0$ vpm. A stainless steel UHV inlet system was used and reduction valves were avoided for the sake of cleanliness. The gas doses are given in units of langmuir (1 L=1.33×10^{-6} mbar s). During the dosing of N$_2$, the ionization gauge and all other filaments were switched off and the chamber was shut off from the turbomolecular pump by a metal valve to allow for high dosing pressures. The pressure was measured by a rotating ball pressure gauge (Leybold Heraeus Viscovac VM 211) which allowed pressure readings up to 2 mbar. A maximum dosing pressure of about 1 mbar was chosen so that the turbomolecular pump could pump down the preparation chamber without being shut off and without using a bypass roughing line. Coverages are given relative to the number of substrate surface atoms throughout the paper. As can be seen from Fig. 1, the number of atoms in the uppermost surface layer strongly decreases as the different surfaces become more open: 15.7×10^{14} cm^{-2} [Ru(0001)], 8.62×10^{14} cm^{-2} (Ru(10$\bar{1}$0)), and 4.72×10^{14} cm^{-2} (Ru(11$\bar{2}$1)). The sample was kept at room temperature during dosing of N$_2$.

III. RESULTS

Since the sticking coefficient for the dissociative nitrogen adsorption on Ru single crystals is extremely small, contamination by spurious amounts of other gases like CO or hydrogen causes serious problems. These problems could be largely circumvented by the cleanliness achieved by the experimental setup described above. For the results to be discussed in this contribution we have identified the adsorbed species by HREELS and evaluated their quantity by TDS. In the following, two representative results are discussed which are measured on Ru(0001).

A. N$_2$ dissociation on Ru(0001)

Figure 2 exhibits a HREEL spectrum recorded after exposing the Ru(0001) surface to 3.1×10^9 L of N$_2$ (experiment B in Table I). Only two losses are present in this spectra, one at 54.6 meV and one at 245.55 meV. They can be easily assigned to the Ru–CO and the C–O stretch vibrations. It is known that the energy of the C–O stretch vibration ν(C–O) shifts with coverage.[26] In a separate experiment we correlated the energy of ν(C–O) with the CO coverage as determined by TDS. The CO saturation coverage θ_{CO}^{max} (300 K) =0.56 was determined by calibration against the value of θ_{CO}^{max} (100 K)=0.68 from Ref. 27. Comparing the loss energy of 244.55 meV with these CO adsorption data yields a CO coverage of 0.02 for the spectrum of Fig. 2. Only a very faint peak is visible at 71 meV where the Ru–N stretch vibration is expected.[22] A N coverage of 0.05 gives rise to a pronounced peak at 71 meV. Therefore, we estimate $\theta_N \leqslant 0.02$ from the HREEL spectrum of Fig. 2. To determine a more exact value we have to use TDS as discussed in the following.

For the same experiment Fig. 3 exhibits the TD spectra of masses 2, 14, and 28. Note that the intensities of masses 2, 14, and 28 are scaled so that the intensity maxima have about the same height. The TD spectrum of mass 2 shows a peak at 350 K which is due to hydrogen desorption.[12] At 480 K peaks of mass 14 and mass 28 are visible, while at 900 K there is only a peak in the mass 14 signal. The peak at 480 K

TABLE I. N₂ dose in units of langmuir (1 L=1.33×10⁻⁶ mbar s), relative coverages θ_i (i=CO, H, N) as determined through HREELS or TDS, N₂ pressure p (mbar), dosing time t (min), and initial sticking coefficient s_0 for dissociative N₂ adsorption for a number of experiments A–H. The experiments were performed at 300 K.

	N₂ dose (L)	θ_{CO} HREELS	θ_{CO} TDS	θ_H TDS	θ_N TDS	p (mbar)/ t (min)	s_0
	Ru(0001)						
A	5.8×10^8	0.2	0.04	0.04	0.005	0.43/30	1×10^{-11}
B	3.1×10^9	0.02	0.04	0.02	0.002	0.57/120	1×10^{-12}
C	6.8×10^9	0.2[a]	0.07[a]	0.06[a]	0.005	0.15/1000	2×10^{-12}
	Ru(10$\bar{1}$0)						
D	2.0×10^9	0.4	⋯	⋯	<0.05[b]	0.63/70	4×10^{-11}
E	3.5×10^{10}	<0.5	⋯	⋯	<0.05[b]	0.7/1067	2×10^{-12}
F	2.3×10^{11}	0.1	0.2	0.14	0.08	1.26/4100	4×10^{-13} [c]
	Ru(11$\bar{2}$1)						
G	2.0×10^8	0.4	0.46	d	0.006	0.001/4290	2×10^{-11}
H	6.7×10^{10}	0.4	0.46	<0.02	0.028	0.275/5400	3×10^{-13} [c]

[a]After HREELS and before TDS annealed to 550 K.
[b]From HREELS.
[c]Observation of subsurface N.
[d]Not measured.

is due to the known desorption of small amounts of CO. The TD spectra of CO/Ru(0001)[27] show a pronounced broadening of the desorption peak with increasing coverage. Contrary to the absolute value of the TDS integral, which is very sensitive to the position of the sample relative to the mass spectrometer, the width of the TDS peaks is not and therefore is a sensible measure for the amount of desorbing CO, especially for small amounts of CO. From the width of the CO TD spectrum in Fig. 3 a CO coverage of 0.04 was determined. The difference of CO coverages, as determined by HREELS and TDS, results from an instrumental effect of the TDS measurements. In order to detect smallest amount of N₂, the sample was placed directly in front of the mass spectrometer, thereby increasing the CO partial pressure inside the spectrometer due to reduced pumping speed, so that additional CO was adsorbed on the sample before the CO de-
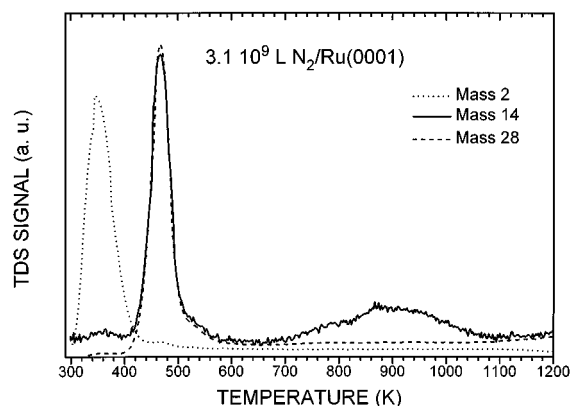
sorption temperature was reached. For this reason, the CO coverage determined by TDS is always higher than the coverage determined by HREELS. The different cracking patterns for CO and N₂ (CO: mass 28/mass 14=100/0.8; N₂: mass 28/mass 14=100/14) allow one to clearly distinguish between CO and N₂ desorption. In this manner, the TDS peak at 900 K could be assigned to the desorption of small amounts of N₂. The TD spectrum of mass 28 does not show a peak at 900 K because of the large background for mass 28 due to CO, whereas the background for mass 14 is small. A good estimate for the amount of N₂ could be made by comparing the TDS integrals of mass 14 of the CO and N₂ desorption peaks. Using the cracking pattern, the coverage of N could be determined to $\theta_N\approx0.002$. This is in good accordance with the high desorption temperature since in our earlier study[22] there was only a very weak signal extending to temperatures as high as 900 K. The value of $\theta_N\approx0.002$ also agrees with the estimation made from the HREELS result.

In order to evaluate the sticking coefficient for dissociative adsorption of N₂, the area of the surface that was covered with CO or hydrogen during the N₂ exposure was taken into consideration in the following way. Since for small coverages the coverage of CO and hydrogen increases linearly with time, half of the CO and hydrogen covered surface was subtracted from the total surface area. In this way, a N₂ sticking coefficient of 1×10^{-12} was determined for the dose of 3.1×10^9 L N₂, i.e., experiment B for which the spectra are shown in Figs. 2 and 3. The coverages and sticking coefficients derived for a number of different exposures are summarized in Table I. In addition, Fig. 4 exhibits the sticking coefficients derived for the three different Ru surfaces and for different N₂ doses.

From the measurements for Ru(0001) in Fig. 4 one recognizes that the sticking coefficient is on the order of 10^{-12}. The measurements were limited by the contamination of CO adsorption. Exposing the surface to 6.8×10^9 L N₂ resulted in

FIG. 3. TD spectra for Ru(0001) exposed to 3.1×10^9 L N₂ at 300 K, measured after the HREEL spectrum depicted in Fig. 2. The intensities of the different masses are scaled to match. The peaks of masses 14 and 28 at 480 K are due to CO desorption, the peak of mass 14 at 900 K is due to nitrogen desorption.
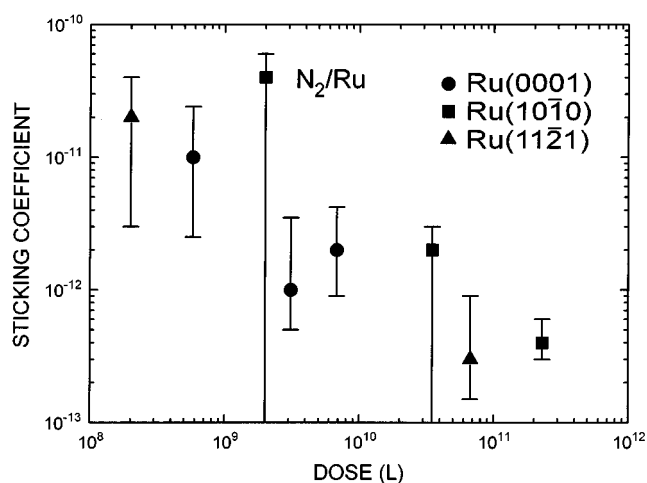
FIG. 4. Sticking coefficients for dissociative adsorption of N$_2$ on Ru(0001) for different exposures of N$_2$ in units of langmuir (1 L=1.33×10^{-6} mbar s). The error bars reflect the uncertainty of the desorbing amount of N$_2$.

a CO coverage θ_{CO}=0.2; 2.6×10^{10} L N$_2$ resulting in θ_{CO}=0.45 near the saturation value of 0.56. Since it is reasonable to assume that the adsorbed CO blocks sites for the N$_2$ dissociation, we approached the limit of feasibility of our experiment at doses of about 10^{10} L. The experiment with the 2.6×10^{10} L dose was therefore not included in Table I and Fig. 4. Finally, we note that Fig. 4 is not meant to imply that s depends on dose. Figure 4 only shows in which range of doses we approach the true value of s_0. At smaller doses the value should be considered as an upper limit.

In the TDS analysis of the amount of adsorbed N we relied upon the known value of θ_{CO}^{max}. For the HREELS analysis we had to know the maximum coverage of N. For this reason, we prepared a saturated N layer and determined its value through TDS by comparison with CO. We evaluated θ_N^{max}=0.25. After cooling to 100 K we could observe a 2×2 LEED pattern which compares well with θ_N=0.25. The LEED pattern was independent of preparation, which was ionization gauge-assisted adsorption (500 K, 1×10^6 L) as well as NH$_3$ decomposition (500 K, 6×10^3 L). We also observed that the rate for cooling below 300 K should not be too large. A cooling rate of 0.2 K/s was small enough to prepare a 2×2 LEED pattern. For a rate of about 2 K/s a pattern with a ringlike structure connecting the 2×2 superstructure spots was observed.

B. N$_2$ dissociation on Ru(10$\bar{1}$0)

The sticking coefficient of N$_2$ on Fe increases for the more open Fe surfaces.[4,5] Therefore, similar experiments as described above for Ru(0001) were carried out using a Ru(10$\bar{1}$0) surface. Detailed results of the vibrational spectrum of N/Ru(10$\bar{1}$0) will be presented elsewhere.[28] Here we mention only the following: Exposing the surface to 10^6 L N$_2$—with the ionization gauge switched on—led to a saturation of the surface with N. The HREEL spectrum exhibited two vibrational losses at 40 and at 60 meV. A $\left(\begin{smallmatrix} -1 & 1 \\ 2 & 1 \end{smallmatrix}\right)$ LEED pattern was observed. For CO we assumed θ_{CO}^{max}=1.2 accord-

ing to Ref. 29. Comparing integrated TDS signals from surfaces saturated by N and by CO yielded a saturation coverage for N of θ_N=0.67. The TDS peak shifted with increasing coverage from 700 to 640 K, indicating a thermally destabilized Ru–N bond on Ru(10$\bar{1}$0) as compared to Ru(0001).

In order to further probe whether the surface was covered by some adsorbates difficult to detect by HREELS after the very high N$_2$ doses of experiments D and E, we dosed an additional amount of 10^6 L N$_2$ with the ionization gauge switched on. We found dissociative N$_2$ adsorption identical to that found for the bare surface and concluded that there were no "invisible" adsorbates. Because of this modification of the experiment the amount of chemisorbed N was estimated only from the HREEL spectra (see Table I). We found no N signal in the HREEL spectra. From our ionization gauge-assisted adsorption experiments[28] we noticed that θ_N=0.05 can easily be detected with HREELS. Our estimate of θ_N<0.05 for experiments D and E is therefore conservative. The resulting sticking coefficients are upper limits for the same reason. In experiment F the surface was exposed to 2.3×10^{11} L N$_2$, then a HREEL spectrum was taken and the amount of adsorbed N was determined by TDS. The energy of the C–O stretch mode and its intensity indicated a CO coverage of 0.1 ML. Experiment F is of the highest cleanliness we could achieve. By comparison of the CO and N integrated TDS intensities θ_N=0.08 and s_0=4×10^{-13} were derived. However, although the N coverage was large enough so that N should be visible in HREELS, no Ru–N loss was found, indicating that N is mainly in a subsurface position. This is confirmed by the observation that the TDS peak is shifted to a higher temperature by about 110 K compared to the desorption of surface N.[28]

C. N$_2$ dissociation on Ru(11$\bar{2}$1)

In varying the morphology of the surfaces under investigation we stepped further to the Ru(11$\bar{2}$1) surface. As can be seen from Fig. 1, the ideal, bulk-truncated Ru(11$\bar{2}$1) surface is much more open and exposes a variety of different adsorption sites. The preparation of this surface, which has not been studied up to now, will be discussed in the context of a future discussion of CO adsorption on Ru(11$\bar{2}$1).[28] The clean Ru(11$\bar{2}$1) surface exhibited a sharp 1×1 LEED pattern after a number of sputter-anneal cycles. So far, we have not been able to observe any ordered LEED pattern induced through adsorption of N$_2$, N, or CO. Therefore, we have no numbers for the adparticle densities for CO or for N$_2$. Instead, we derive some numbers by analogy to the more close-packed surfaces. The density of CO within a saturated adsorption layer is 0.85×10^{15} cm^{-2} for Ru(0001) and 1.0×10^{15} cm^{-2} for Ru(10$\bar{1}$0). The same density would be equivalent to a coverage of θ_{CO}=2 on Ru(11$\bar{2}$1). The N covered Ru(11$\bar{2}$1) surfaces were prepared by decomposition of NH$_3$ (Ref. 30) and by ionization gauge-assisted N$_2$ dissociation. As expected from the surface morphology, the HREELS spectra of chemisorbed N are very complicated with peaks at 50, 60, 69, and 75 meV. In TDS the peak maximum shifts from 700 to 620 K with coverage. Two experiments were
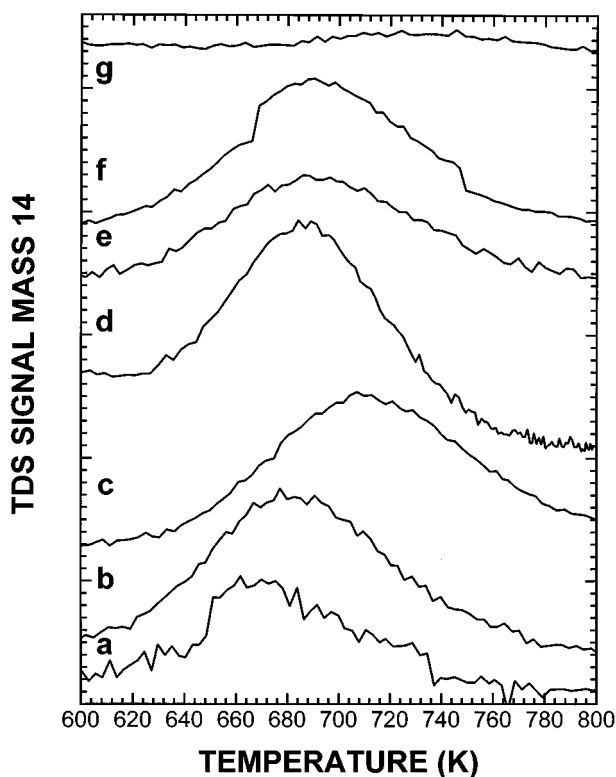
FIG. 5. Integral intensity from the N_2 signal (at mass 14) for a Ru($11\bar{2}1$) surface exposed once to 6.7×10^{10} L N_2 at 300 K. Spectrum a was measured after the adsorption with a maximum temperature during the recording of 990 K, spectrum b was taken 125 min later with a maximum temperature of 890 K, spectrum c 1170 min later with a maximum temperature of 1020 K, spectrum d was taken 120 min later with a maximum temperature of 800 K, spectrum e was taken 30 min later with a maximum temperature of 930 K, spectrum f was taken 150 min later with a maximum temperature of 1100 K, spectrum g was taken 30 min later.

performed to study N_2 dissociation on Ru($11\bar{2}1$), the data of which are included in Table I. Coverages are estimated assuming particle densities similar to Ru(0001) and Ru($10\bar{1}0$) as mentioned above.

Two main conclusions can be drawn from the Ru($11\bar{2}1$) data shown in Table I: (1) The mean sticking coefficient for N_2 dissociation is not enhanced on the more open Ru($11\bar{2}1$) surface. (2) It may well be instead that the formal sticking coefficient is even lower than for the other surfaces. The latter point is very surprising and is commented on further in the following. Figure 5 shows the amount of desorbed N_2 from integration of the mass 14 TD spectra from a series of different surface treatments after exposing the surface to 6.7×10^{10} L N_2. Spectrum a was recorded immediately after dosing, and a small amount of N_2 desorbs at 670 K. One-hundred-twenty-five min later, spectrum b was recorded after dosing 10 L CO to calibrate the TDS integrals. On a clean surface this CO dose saturates the surface, but comparing the shape of the TD spectra indicated that only 8% of the saturation coverage of CO was adsorbed on the surface. Again N_2 desorption was observed. Spectrum c was recorded the next day, i.e., 1170 min later, and still desorbing N_2 was found; spectrum d, recorded 120 min later, again shows N

desorption. Half an hour later, spectrum e still shows N_2 desorption. A HREEL spectrum recorded at this time showed losses that indicated an O coverage equivalent to 0.3 L O_2 which gives rise to a very small O coverage most likely due to dissociation of CO.[28] One-hundred-fifty min later, spectrum f was recorded showing again N_2 desorption, even spectrum g, recorded 30 min later, still shows small traces of nitrogen. Adding the TDS integrals of spectra a–f results in an amount of N_2 which is nine times larger than the amount of N_2 desorbing in the TDS directly after the N_2 dosing. No systematic dependence on the time elapsed between the measurements or the temperature up to which the sample was heated during the experiments could be detected. These experiments clearly indicate that atomic nitrogen is dissolved into the bulk. This also explains the formally small sticking coefficient which is calculated from the amount of N found on top of the surface in HREELS or which evolves in one single TDS run after dosing.

IV. DISCUSSION

It is known that the sticking coefficient s for dissociative adsorption of N_2 on Ru(0001) is very small, i.e., practically zero in the sense that up to now it was not possible to cover any single-crystalline Ru surface with N by dosing N_2 under UHV conditions. There was a number of $s < 10^{-8}$ quoted by Matsushima as a result of an indirect estimate.[13] The main result of our work is that we have been able to measure the value of the sticking coefficient, which is as small as $s_0 \approx 1 \pm 0.8 \times 10^{-12}$ at room temperature. The error limits are estimated from the scatter of the data points. Even at those high exposures which we used in our experiment, we are not able to adsorb more than some percent of a monolayer of N. Therefore, the sticking coefficient determined in our experiment is the sticking coefficient at small N coverage, i.e., the initial sticking coefficient s_0. Generally, it is well known that s may change with coverage.

There are two main limiting factors which prevent us from measuring even smaller values: (1) blocking of the surface by foreign atoms from the residual gas, and (2) dissolution of N within the subsurface region. First, we comment on the surface blocking by residual gases which consist of H_2, CH_4, CO, H_2O, and spurious amounts of rare gases and higher hydrocarbons. From these species only H_2 and CO are known to stick to the Ru surface at room temperature or above. The adsorption of both H and CO could be easily controlled by HREELS and TDS, and the respective coverages are quoted in Table I. For the very clean UHV system described above this small amount of contamination is not surprising, considering the order of magnitude of the partial pressures involved. Disconnecting the chamber from the turbopump by the metal valve induces a pressure increase up to 10^{-9} mbar within 10 min. A residual gas analysis, however, indicates that this is mainly CH_4, very likely released from the Ti films of the Ti sublimation pump (TSP). The main source of contamination certainly is the dosing gas N_2 itself whose cleanliness is specified as 99.999 90%. If we fill the preparation chamber with N_2 up to 1 mbar, we introduce at

least 1×10^{-6} mbar of other gases. This is not as much as it may appear at a first glance. First, the residual gases are only in part chemically active; the CO partial pressure, for example, is specified so that it contributes only 10^{-7} mbar. Second, the TSP is capable of pumping 10^{-2} mbar of active gases if a new Ti film is prepared. Here it becomes also clear that the state of the TSP may be responsible for the fluctuations in the final amount of H and CO for the different experiments which can be seen from Table I. These considerations give some plausibility as to why we could apply such large gas doses under UHV conditions.

Second, we comment on the dissolution within the bulk: For the more open Ru($10\bar{1}0$) and Ru($11\bar{2}1$) surfaces we have observed that small amounts of nitrogen are released from the subsurface region. This effect could in principle make our experiment unfeasible since we extract the number of dissociated molecules from the species adsorbed on the surface as seen by HREELS and from a single temperature scan in TDS, assuming desorption from the adsorption layer. For our measurements the effect of dissolution of N into the bulk, although detectable, is very small. Only for 6.7×10^{10} L dosed to Ru($11\bar{2}1$) have we observed a measurable effect in TDS, as discussed in the context of Fig. 5. The first TD spectrum gives $\theta_N=0.0028$, and all seven TD spectra together give $\theta_N=0.03$, which is still only some percent of a monolayer. We believe that for N$_2$ doses $>10^{11}$ L diffusion into the bulk sets a limit for our measurements. For these high doses one had to sample the N out of the bulk through a number of TDS scans. This introduces additional uncertainties, and we stopped the experiment here. For the Ru($10\bar{1}0$) surface the TDS peak of the presumable subsurface N is shifted by 110 K to higher temperatures, whereas such a shift is not observed for Ru($11\bar{2}1$). This observation has to be explained in future studies.

Since the determination of s_0 within our UHV experiment is at the borderline of its feasibility, it is very important to have some comparison with other methods. Recently, a real Ru catalyst supported by MgO was studied by Rosowski *et al.* in a flow experiment using a microreactor.[31] Such an experiment has advantages and disadvantages compared to an UHV experiment. The advantage of such an experiment is that very high doses can be applied. Saturation with chemisorbed atomic N was achieved by flowing N$_2$ at a pressure of 1 bar for 14 h over the catalyst which was held at 573 K. The amount of adsorbed N was determined in a TDS experiment in which a N$_2$ transient within the He carrier gas is detected during a temperature increase of the catalyst. The dose applied in the 14 h experiment amounts to 4×10^{13} L, but 80% of the N saturation value was already attained for 2×10^{12} L. Microkinetic modeling leads to a sticking coefficient of about 5×10^{-12} at 573 K. This value drops to about 1×10^{-14} at 300 K. On the other hand, a linear extrapolation of the data between 470 and 670 K to 300 K gives a value of about 1×10^{-13}. This value is in accordance with our result, considering the error bars of both experiments. The error bar for the flow experiment is largest at 300 K. The deviation to smaller values at 300 K in the flow experiment may be due to site blocking by chemisorbed H which can migrate

through the catalyst sample via desorption and readsorption at 300 K. For comparison, CO is thought to be trapped in the outer layer when entering the catalyst sample. We also mention that 300 K is the only temperature for which we can compare both experiments since in the UHV experiment the gas temperature stays at 300 K when the sample is heated to higher temperatures, whereas in the flow experiment gas-phase molecules and catalyst are at the same temperature.

The microkinetic analysis of the TDS data of the flow experiment revealed an activation barrier of 27 kJ/mol for the dissociative adsorption of N$_2$. The existence of such an activation barrier is consistent with the low value of the sticking coefficient, but any quantitative microscopic understanding is waiting for further experiments and theoretical analysis.

One problem in discussing the flow experiment is related to the fact that the morphology of the Ru surfaces is not known. Therefore, the basis for any meaningful comparison between UHV and flow experiments is our observation that the sticking coefficient is independent of surface morphology within about a factor of 2.

The value of $s=2\times10^{-6}$ found for ionization gauge-assisted adsorption[22] is six orders of magnitude larger than the value found for thermal ground-state molecules. It is evident that this process has completely concealed the properties of the adsorption process of thermal ground-state molecules. It was found that the ionization gauge-assisted adsorption is independent of the sample temperature between 420 and 700 K and was not even influenced by submonolayer amounts of Cs other than by purely geometric site blocking. These observations now become quite reasonable, considering that the whole process is governed by the degree of excitation of the N$_2$ molecules. If the adsorption process is extremely favored for vibrationally excited molecules, we expect that the surface temperature may have an influence on the adsorption of thermal ground-state molecules. This may be in line with the fact that the maximum NH$_3$ production is found at about 620 K for an unpromoted Ru catalyst.[32] Besides the influence of temperature we also have to check again the influence of the Cs promoter in our ongoing experiments.

For the saturated N layer we have found $\theta_N^{max}=0.25$. This value is in accordance with the 2×2 LEED pattern observed at 90 K. It corrects our value of 0.5 given recently.[22] In Ref. 22 we calibrated the N$_2$-TDS signal by using the signal from the $(\sqrt{3}\times\sqrt{3})R30°$ structure of chemisorbed N$_2$ at 100 K. Difficulties in preparing a $\sqrt{3}$ structure with $\theta_{N_2}=0.33$[33,34] and the less refined TDS measurements in the previous work may have introduced this error. A 2×2 structure has been found after NH$_3$ decomposition by Danielson *et al.*[12] Our finding of a 2×2 LEED pattern is also in very good agreement with a recent scanning tunneling microscopic investigation in which a majority of 2×2 distances, nearly no $\sqrt{3}$ distance, and only very small 2×2 patches, i.e., no long-range order, has been found at 300 K.[35]

With respect to the small value of s_0 one can ask whether or not the surface imperfections like point defects or steps may influence or even dominate the N$_2$ dissociation. An

answer to this question can be given from a recent scanning tunneling microscopic investigation of the dissociation of N_2 on Ru(0001): no indication of a preferred adsorption near to edge sites has been found.[35]

V. CONCLUSION

We have shown that the initial sticking coefficient for dissociative adsorption of N_2 at 300 K is $s_0 = (1 \pm 0.8) \times 10^{-12}$ for Ru(0001), Ru(10$\bar{1}$0), and Ru(11$\bar{2}$1). Within the limits of our experiment s_0 is independent of surface orientation. Future microkinetic modeling of the NH_3 synthesis on Ru surfaces has to take this surprising low value into account. For Ru(10$\bar{1}$0) and Ru(11$\bar{2}$1), subsurface N was observed. Following preparation by NH_3 decomposition at 500 K or ionization gauge-assisted dissociation of N_2 at 500 K, a N coverage of 0.25 was found. The N layer gives rise to a 2×2 LEED pattern at a sample temperature of 90 K but is disordered at 300 K.

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