

Vibrations, coverage, and lateral order of atomic nitrogen and formation of NH_3 on $\text{Ru}(10\bar{1}0)$

Cite as: J. Chem. Phys. **106**, 9313 (1997); <https://doi.org/10.1063/1.474042>

Submitted: 02 January 1997 . Accepted: 20 February 1997 . Published Online: 04 June 1998

H. Dietrich, K. Jacobi, and G. Ertl



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Coverage, lateral order, and vibrations of atomic nitrogen on \$\text{Ru}\(0001\)\$](#)

The Journal of Chemical Physics **105**, 8944 (1996); <https://doi.org/10.1063/1.472624>

[Dissociative chemisorption of nitrogen on \$\text{Ru}\(0001\)\$](#)

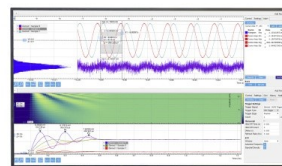
The Journal of Chemical Physics **99**, 9248 (1993); <https://doi.org/10.1063/1.465541>

[Interaction of hydrogen with nitrogen atoms chemisorbed on a \$\text{Ru}\(0001\)\$ surface](#)

The Journal of Chemical Physics **102**, 1432 (1995); <https://doi.org/10.1063/1.468930>

Challenge us.

What are your needs for
periodic signal detection?



Zurich
Instruments



Vibrations, coverage, and lateral order of atomic nitrogen and formation of NH₃ on Ru(1010)

H. Dietrich, K. Jacobi, and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

(Received 2 January 1997; accepted 20 February 1997)

The dissociative chemisorption of nitrogen on the Ru(1010) surface has been studied using high-resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and low-energy electron diffraction (LEED). To prepare a surface covered by atomic nitrogen we have used ionization-gauge assisted adsorption. A saturation coverage of $\theta_N=0.6$ is achieved of which about 30% is in the subsurface region. At saturation coverage a $\begin{pmatrix} -1 \\ 2 \\ 1 \end{pmatrix}$ LEED pattern is observed. The $\nu_{\parallel}(\text{Ru-N})$ mode at 41 meV and the $\nu_{\perp}(\text{Ru-N})$ mode at 60 meV are identified. Upon exposing the nitrogen covered surface to hydrogen at 300 K we have observed the formation of NH₃ which is characterized by its symmetric bending mode $\delta_s(\text{NH}_3)$ at 149 meV. At 400 K, NH₃ could not be detected. The reaction intermediate NH is stable up to 450 K and has been identified by its vibrational losses $\nu(\text{Ru-NH})$ at 86 meV, and $\nu(\text{N-H})$ at 408 meV. The TD spectra of mass 14 show three desorption states of nitrogen, N_{α} at 740 K (from subsurface N), N_{β} shifting from 690 to 640 K with increasing coverage, and N_{γ} at 550 K. The activation energy for desorption via the N_{β} state is 120 ± 10 kJ/mol. The TD spectra of mass two showed three desorption states at 450, 550, and 650 K due to the decomposition of NH_x. © 1997 American Institute of Physics. [S0021-9606(97)01220-8]

I. INTRODUCTION

The synthesis of ammonia from nitrogen and hydrogen on iron catalysts (the Haber-Bosch process) is a very important industrial catalytic process. The underlying reaction mechanism consists of the dissociative chemisorption of N₂ followed by hydrogenation of N on the surface.^{1,2} There has been a continuous interest in ammonia synthesis on transition metal surfaces in order to elucidate the catalyst's influence on the reaction pathway. Several groups have studied Ru catalysts which may replace Fe as the catalyst for ammonia synthesis.³⁻⁵ The reaction mechanism of the Ru-based catalyst is not yet completely established, and it is our aim to contribute to a better understanding of the processes involved. The first step of ammonia synthesis is the dissociative adsorption of nitrogen for which the initial sticking coefficient, s_0 , was found to be extremely low at room temperature ($s_0=1 \times 10^{-12}$) and independent of surface orientation on Ru(0001), Ru(1010), and Ru(1121).⁶ The next step of the reaction, the hydrogenation of chemisorbed atomic nitrogen, has been studied by Shi *et al.* on Ru(0001).⁷

Chemisorbed atomic nitrogen on a Ru surface can be prepared by electron bombardment,^{8,9} by plasma discharge¹⁰ of molecular nitrogen, by high doses of nitrogen with the ionization gauge switched on,⁶ by dosing extremely high doses of molecular nitrogen,⁶ or by dissociation of NH₃,^{8,11} N₂H₄,¹² or NO.¹³⁻¹⁵ We choose ionization-gauge assisted adsorption since this method produces a very clean nitrogen layer, and no NH_x species are involved in or left over from the production of the adlayer as may be the case for the decomposition of NH₃ or N₂H₄. With this method we were able to monitor the synthesis of NH, NH₂, and NH₃. The direct formation of NH_x in a surface reaction between ad-

sorbed nitrogen and hydrogen has been reported previously only for Ru(0001).⁷

To identify different NH_x species adsorbed on the Ru(1010) surface, we make use of the existing data on the interaction of NH₃ with Ru(0001) and Ru(1121). The characteristic feature of a HREEL spectrum of NH₃ adsorbed on Ru(0001) or Ru(1121) is the umbrella mode at 144 meV¹⁶⁻¹⁸ in the low-coverage limit. Ammonia is stable up to 300 K on Ru(0001)⁷ and up to 310 K on Ru(1121).¹⁷ The reaction intermediates NH and NH₂ were monitored on Ru(0001) and on Ru(1121). The vibrational characteristics of NH chemisorbed on Ru(0001) are the three losses $\nu(\text{Ru-NH})$, $\delta(\text{NH})$, and $\nu(\text{N-H})$ at 86, 166, and 410 meV, respectively. About the same frequencies were found for Ru(1121). NH₂ was identified on Ru(1121) by the $\delta(\text{NH}_2)$ mode at 189 meV and the $\nu_a(\text{N-H})$ mode at 419 meV. Recently, LEED intensity analysis of the 2×2 and $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures has shown that atomic nitrogen adsorbs at the Ru(0001) hcp three fold-hollow sites.¹⁹

Here we report on the adsorption of nitrogen on Ru(1010) at different surface temperatures. At 300 K we monitored the formation of NH₃ and NH; at 450 K only NH was synthesized. Part of the adsorbed nitrogen diffuses into the subsurface region.

II. EXPERIMENTS

The experiments were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure of 1×10^{-11} mbar. The apparatus consisted of two chambers: the upper chamber contained an argon ion gun, a quadrupole mass spectrometer, and a LEED optics; the lower chamber housed a high-resolution electron energy loss spectrometer (HREELS) for recording vibrational spectra. The two cham-

bers were separated by a valve in order to keep the lower chamber at a pressure of 3×10^{-11} mbar during preparation of the sample in the upper chamber. The HREEL spectrometer was developed and mounted in the laboratory of Ibach.²⁰ HREEL spectra were taken at a 60° angle of incidence with respect to the surface normal and in specular geometry. The primary energy was 2.5 eV and the energy resolution was set to 3.4 meV. Typically, count rates in the elastic peak of about 3×10^5 counts/s were achieved. The typical working pressure after large N_2 doses was 1×10^{-10} mbar.

The mass spectrometer was used to perform TDS measurements 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. The signals for m/e ratios of 2, 14, 17, and 28 were recorded quasi-simultaneously to follow the desorption of hydrogen, nitrogen, ammonia, and CO. The cracking pattern of N_2 and CO differ for mass 14 and, therefore, allow CO and N_2 desorption to be distinguished. The Ru(10 $\bar{1}$ 0) single crystal was 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 upper edge of the sample. Cleaning of the surface was achieved by repeated cycles of sputtering and annealing to 1570 K. The cleanliness of the surface was verified by LEED and HREELS. The purity of the N_2 was 99.9999%. We used a stainless steel UHV inlet system and avoided reduction valves for the sake of cleanliness. The N_2 exposures were performed at partial pressures of $(5-10) \times 10^{-5}$ mbar. The gas doses are given in units of Langmuir ($1 \text{ Langmuir} = 1.33 \times 10^{-6}$ mbar s). Coverages are given relative to the number of substrate surface atoms throughout the paper.

III. RESULTS

A. HREELS

Previously, we have shown that the initial sticking coefficient for the dissociative adsorption of N_2 on Ru single crystal surfaces at 300 K is only $s_0 = 1 \times 10^{-12}$.⁶ Therefore, in order to prepare high coverages of chemisorbed atomic nitrogen, we exposed the surface to high doses of nitrogen with the ionization gauge switched on.^{6,21}

Figure 1 shows a series of HREEL spectra recorded after exposing the surface to various amounts of N_2 . Before the nitrogen was dosed, the sample was always cleaned by annealing to 1070 K in an oxygen pressure of 2×10^{-8} mbar for 120 s followed by two annealing cycles to 1570 K to remove the oxygen. The cleanliness was then verified with HREELS. For all exposures the pressure was kept at 6×10^{-5} mbar. During exposure the ionization gauge was switched on and the sample temperature was kept at 450 K to minimize the adsorption of residual gases such as hydrogen or CO. The HREEL spectra in Fig. 1 are dominated by two losses at 41 and 60 meV, which gain intensity simultaneously with increasing coverage. We attribute both features to chemisorbed atomic nitrogen. Since the two losses at 41

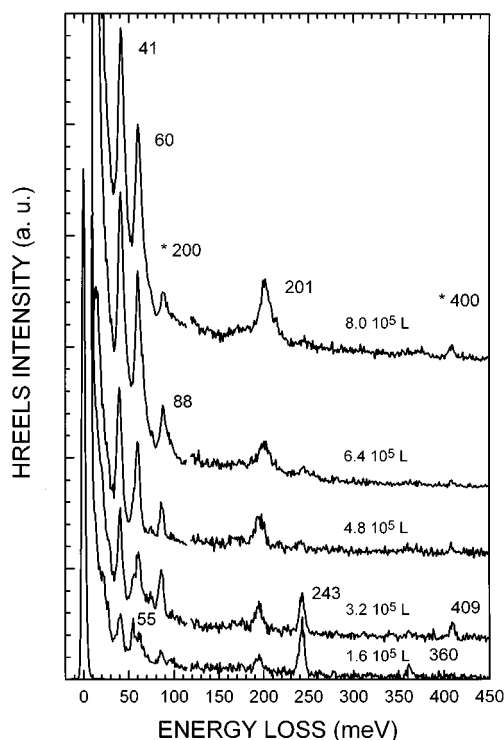


FIG. 1. HREEL spectra for a series of nitrogen exposures on Ru(10 $\bar{1}$ 0) at 450 K. The N_2 exposures are indicated in the plot. The primary energy of the electrons was 2.5 eV and all spectra were recorded in specular geometry with an angle of incidence of 60° with respect to the surface normal.

and 60 meV always appear and disappear together (upon annealing, Fig. 2), it is rather unlikely that they belong to two different surface species. On Ru(0001), N atoms adsorb in hcp threefold-hollow sites.¹⁹ The Ru(10 $\bar{1}$ 0) surface has two different threefold-hollow sites, one fcc like and one hcp like, as shown in Fig. 8 below, which are tilted by 20° with respect to the surface plane of the unrelaxed surface. It is very likely that the chemisorbed nitrogen atom is also tilted with respect to the Ru(10 $\bar{1}$ 0) surface in order to achieve equal bond lengths to its three Ru neighbors. By this tilt the dipole moment of the frustrated translation parallel to the surface gets a component in the direction of the surface normal and, therefore, becomes dipole active. On the basis of this argument we assign the loss at 41 meV to the $\nu_{\parallel}(\text{Ru-N})$ vibration and the loss at 60 meV to the $\nu_{\perp}(\text{Ru-N})$ vibration of nitrogen adsorbed in the hcp threefold-hollow like site. The assignment of the two modes parallel and perpendicular to the surface is further confirmed by a nearest-neighbor force constant model.²² Assuming that nitrogen adsorbs on Ru(10 $\bar{1}$ 0) as on Ru(0001), i.e., in a threefold-hollow site and at the same distance above the surface, all parameters needed to calculate the ratio between the frequency perpendicular and parallel to the surface are known. From this analysis a frequency for $\nu_{\parallel}(\text{Ru-N})$ of 42 meV is derived which strongly supports the proposed adsorption site.

The two losses at 88 and 409 meV in the spectra shown in Fig. 1 are easily identified. Since the vibration at 409 meV

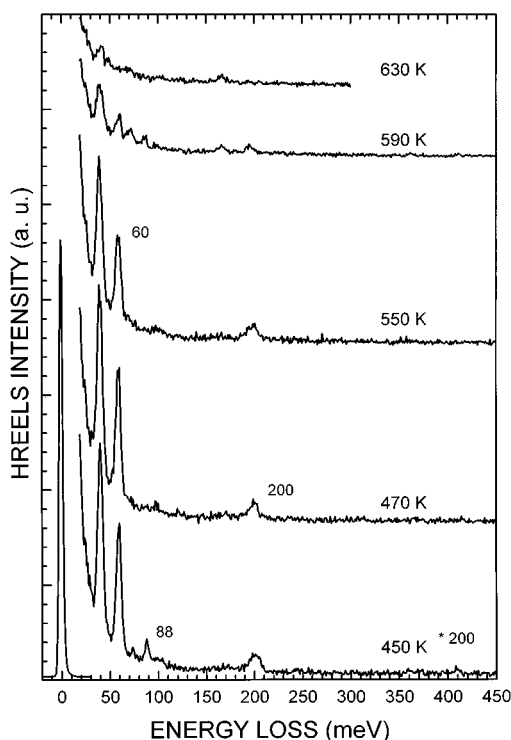


FIG. 2. HREEL spectrum of a nitrogen exposure of 9.5×10^5 L on Ru(1010) at 450 K and the spectra recorded after subsequent annealing to the indicated temperatures. All other parameters are the same as for Fig. 1.

is a very characteristic feature of the $\nu(\text{N-H})$ vibration, we conclude that NH is present on the surface. By comparison with the vibrational energies of $\nu(\text{Ru-NH})$ on Ru(0001) (85 meV) and on Ru(11 $\bar{2}$ 1) (84 and 89 meV) we assign the loss at 88 meV to the $\nu(\text{Ru-NH})$ mode. The $\delta(\text{NH})$ mode which is expected at 166 meV is not observed, thus indicating that NH is adsorbed in an upright geometry.¹² Note that the intensities of the NH related modes do not systematically increase with nitrogen coverage. At low exposures (1.6×10^5 and 3.2×10^5 L) contamination by CO gives rise to the $\nu(\text{Ru-CO})$ vibration at 55 meV and the $\nu(\text{C-O})$ vibration at 243 meV. At higher exposures of N₂ no contamination of CO is detected; hence, during dissociative chemisorption of N₂, CO is removed from the surface. A further contamination, which only appears in the spectra recorded after exposing the surface to 1.6×10^5 L, can be identified as CH with the $\nu(\text{C-H})$ vibration at 360 meV.

The loss at 200 meV remains to be identified. A loss with this energy is most likely to originate from an internal vibration of an adsorbed molecule. The loss energy is similar to that corresponding to the $\delta(\text{NH}_2)$ mode, which is found at 189 meV on Ru(11 $\bar{2}$ 1)¹⁷ and at 196 meV on Ru(0001).¹² Three other losses are expected with the appearance of NH₂; the $\nu(\text{Ru-NH}_2)$ mode at 64 meV, the $\nu_s(\text{N-H})$ mode at 408 meV, and the $\nu_a(\text{N-H})$ mode at 419 meV. The $\nu(\text{Ru-NH}_2)$ at 64 meV may be hidden by the $\nu(\text{Ru-N})$ mode. The two high-energy losses, especially the $\nu_a(\text{N-H})$ mode, appear only with a very weak intensity on Ru(11 $\bar{2}$ 1). The intensity of the $\nu_a(\text{N-H})$ mode is found to be about ten

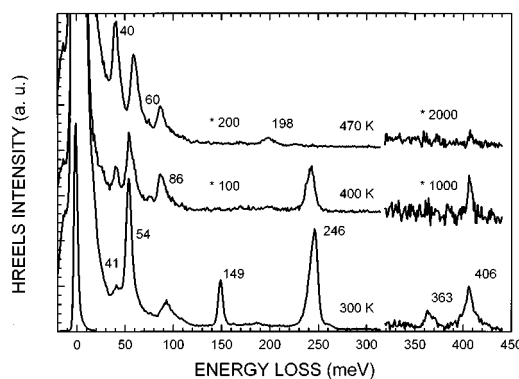


FIG. 3. HREEL spectra for a nitrogen exposure of 8.6×10^5 L N₂ on Ru(1010) at 300 K followed by annealing to the indicated temperatures. All other parameters are the same as for Fig. 1.

times smaller than the intensity of the $\delta(\text{NH}_2)$ mode. In Fig. 1 no loss is visible at 419 meV, but the amount of NH₂ may be so small that the $\nu_a(\text{N-H})$ mode does not emerge from the noise. The spectra in Fig. 2 indicate that the loss at 200 meV is visible up to temperatures of 590 K.

Figure 2 shows the HREEL spectrum after dosing 9.5×10^5 L N₂ at 450 K and after subsequent annealing to the indicated temperatures. The two nitrogen related modes disappear simultaneously upon annealing; at 630 K they have almost disappeared.

As seen in Fig. 1 the intensity of the NH related modes does not systematically increase with the nitrogen exposure. On Ru(0001) the synthesis of NH₃ was found to be mainly time dependent;⁷ exposing the nitrogen covered surface to high doses of hydrogen did not increase the rate of the reaction. If one expects the same reaction mechanism for Ru(10 $\bar{1}$ 0), the amount of NH should increase with time and thus with exposure. Fig. 2 shows that NH has decomposed at 470 K. This explains the scatter in the amount of NH on the surface after adsorption at 450 K since close to the decomposition temperature the amount of NH on the surface is mainly governed by the decomposition and not by the synthesis rate.

Figure 3 shows the HREEL spectrum recorded after exposing the surface to 8.6×10^6 L N₂ with the ionization gauge switched on while the sample was kept at 300 K, and the spectra recorded after annealing to the indicated temperatures. The dosing time was 4 h. The spectrum recorded directly after the nitrogen exposure shows two intense losses at 54 and 246 meV due to CO contamination. The $\nu_{\parallel}(\text{Ru-N})$ mode at 41 meV is still visible, while the $\nu_{\parallel}(\text{Ru-N})$ mode at 60 meV is hidden in the tail of the $\nu(\text{Ru-CO})$ loss. As in the spectra in Fig. 1 we can identify the NH related losses at 86 and 406 meV. In addition to the losses found in the spectra in Fig. 1 we find another prominent loss at 149 meV. The umbrella mode at 144 meV is found to be the most intense loss of ammonia chemisorbed on Ru(0001) and Ru(11 $\bar{2}$ 1). By analogy, we assign this loss to the $\delta_s(\text{NH}_3)$ mode of NH₃. The observation of ammonia after dosing nitrogen at a sample temperature of 300 K proves that ammonia is readily

synthesized. The same process was monitored on Ru(0001). A nitrogen covered surface was prepared at 420 K at which temperature NH₃ is not stable. Then the sample was kept at 300 K in a residual gas pressure of 1×10^{-10} mbar for 18 h. Afterwards, NH₃ was detected by HREELS. The intensities of the $\delta_s(\text{NH}_3)$ mode found after this preparation on Ru(0001) and the intensity in Fig. 3 are about the same. Comparing the time, elapsed between the cooling of the Ru(0001) sample to room temperature and the detection of NH₃, with the dosing time on Ru(10 $\bar{1}$ 0), the synthesis of ammonia appears to proceed faster on Ru(10 $\bar{1}$ 0) than on Ru(0001). On the other hand, it may also be possible that an apparent higher reaction rate is caused by a higher background pressure of hydrogen during the nitrogen exposure. Other experiments on Ru(0001) showed that, after preparing a nitrogen coverage of $\theta_N = 0.13$ and exposing the surface to 5×10^{-6} mbar H₂ for 4×10^3 s at 300 K, a small amount of ammonia was synthesized.⁷ Comparing the intensities of the umbrella mode in Fig. 3 with the intensities found on Ru(0001),¹⁶ we estimated the ammonia coverage to be $\theta_{\text{NH}_3} = 0.08$. Annealing the sample to 400 K, the umbrella mode disappears completely while the NH related losses gain intensity. Since the decrease in intensity of the NH₃ mode is accompanied by an increase in intensity of NH we conclude that NH₃ decomposes into NH and hydrogen. Due to the partial desorption of the adsorbed CO, the CO vibrations lose intensity. Further annealing to 470 K leads to the complete desorption of CO, and to a substantial reduction of NH accompanied by an increase in intensity of the nitrogen related losses. Hence, we conclude that NH decomposes into nitrogen and hydrogen. The loss at 198 meV emerges after annealing to 400 K and gains a little intensity after annealing to 470 K. At this temperature the intensity of the $\nu(\text{N-H})$ loss drops almost to zero.

B. Thermal desorption spectroscopy

Figure 4 shows the N₂TD spectra for a series of nitrogen exposures (the same as in Fig. 1) with the inset giving the resulting nitrogen coverages as a function exposure. The coverage after dosing 8×10^5 L is the saturation coverage we achieved at a sample temperature of 450 K. Doses up to 9×10^6 L did not lead to a further increase in coverage. After a dose of 1.6×10^5 L N₂, a desorption peak occurs at 690 K which we call the N_β state. As the exposure is increased, the desorption peaks shift to a lower temperature as expected for second-order desorption. At higher exposures a small shoulder appears at 560 K, which we call the N_γ state. With increasing exposure the N_α state also emerges on the high temperature side of the N_β state. The way the N_α state emerges is rather unusual; although it is thermally more stable than the N_β state it is not fully developed before the N_β state is populated. This indicates that this state is populated only if the coverage of nitrogen on the surface is high, and further that this state is then thermally more stable than the N_β state. Two scenarios could generate such behavior: (1) a reconstruction of the surface by the chemisorbed nitrogen, and/or (2) subsurface nitrogen. The proposition that the

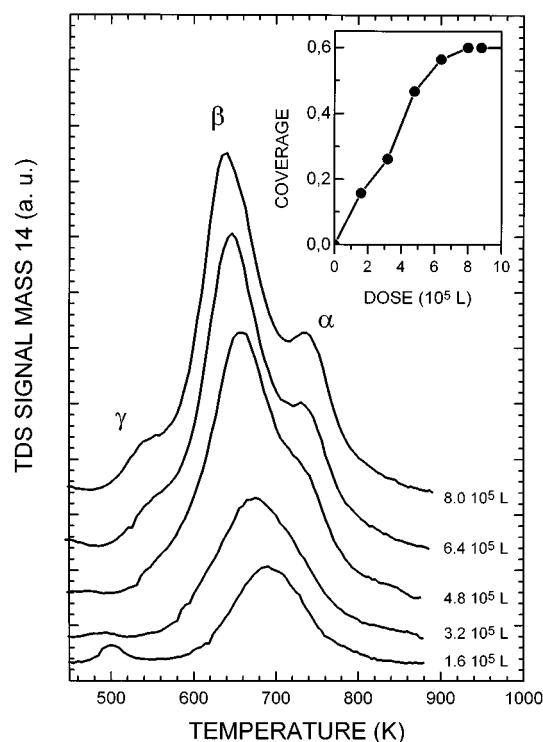


FIG. 4. TD spectra of mass 14 for the series of nitrogen exposures as indicated. The corresponding HREEL spectra are given in Fig. 1. The TD spectra were recorded immediately after the HREEL spectra were taken. The insert gives the coverage as a function of exposure.

desorbing nitrogen of the N_α state originates from subsurface is supported by the HREEL spectra shown in Fig. 2. The nitrogen related losses of the saturation coverage have disappeared after annealing to 630 K. At this temperature only the N_β and N_γ states arising from saturation coverage (Fig. 4) are removed. The N_α state with its peak temperature at 740 K is most likely not affected by an annealing to 630 K. Since we assume that this state is due to the desorption of nitrogen from the subsurface region we do not expect to monitor the $\nu_{\parallel}(\text{Ru-N})$ and the $\nu_{\perp}(\text{Ru-N})$ vibration after annealing to 630 K.

An analysis of the activation energy for the desorption of the N_β state according to the Redhead model for second order desorption,²³ yields an activation energy of $E_{ak} = 120 \pm 10$ kJ/mol. To derive this value we had to assume that the low coverage TD spectra contain no contribution of the subsurface N_α state. Taking a contribution of this state into account would result in a slightly higher activation energy. On Ru(0001), Weinberg and Tsai²⁴ derived a value of $E_d = 184$ kJ/mol, Shi *et al.*²¹ derived 190 kJ/mol, while Rauscher *et al.*¹² found 112 and 120 kJ/mol by two different models.

The total nitrogen coverage was determined to be $\theta_N = 0.6 \pm 0.08$ by comparing the integrated mass 28 TD peak resulting from a saturated monolayer of CO²⁵ with that from the highest nitrogen coverage we achieved. From this coverage calibration we can deduce the initial sticking coefficient of the ionization-gauge assisted adsorption to be about s_0

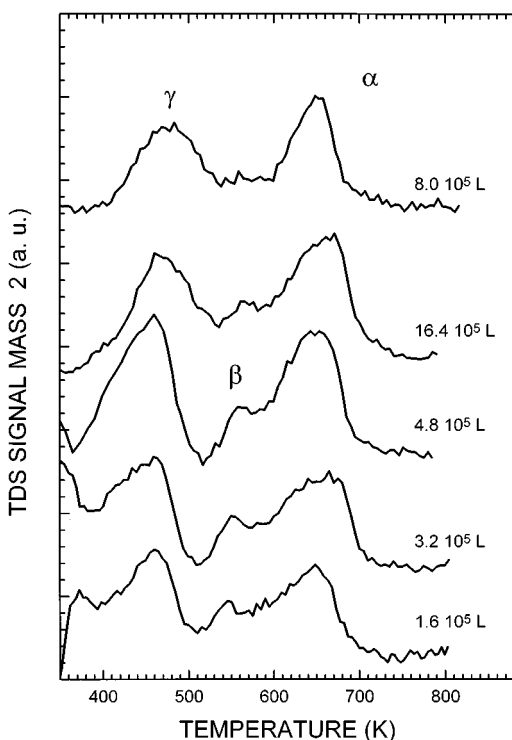


FIG. 5. TD spectra of mass 2 for the series of nitrogen exposures as indicated. The according HREEL spectra are given in Fig. 1. The TD spectra were recorded immediately after the HREEL spectra were taken.

$\approx 1 \times 10^{-6}$. Since the adsorption is governed by the ionization gauge-excited N₂ the sticking coefficient depends somewhat on the position of the sample in the chamber relative to the ionization gauge.

The TD spectra of mass 2 (Fig. 5) were recorded simultaneously with the TD spectra of mass 14 (Fig. 4). The increase in exposure does not lead to an increase in the amount of desorbing hydrogen. Three different desorption states of hydrogen can be distinguished, the H_α state with a peak temperature of 650 K, the H_β state with a peak temperature of 550 K, and the H_γ state at 450 K. The desorption of hydrogen from a surface covered by hydrogen only, is known to be complete by 430 K.²⁶ From the HREEL measurements (Fig. 2) we observe that NH is still detected at 450 K but decomposes upon annealing to 470 K. Hence we assign the H_γ state to the desorption of hydrogen from the decomposition of NH. The amount of hydrogen that desorbs in the H_γ state can be estimated by comparison with the TD spectra of mass 28 (not shown here) taking into account the different ionization probabilities of N₂(1.0) and H₂(0.44). This yields a hydrogen coverage in the H_γ state of $\theta_H = 0.06$ when the surface is saturated with nitrogen. The amount of hydrogen that desorbs from the H_β and the H_α state varies between $\theta_H = 0.07$ and $\theta_H = 0.11$. Due to their high peak temperature, the H_β and the H_α state can only be attributed to the decomposition of an NH_x species, or to hydrogen that originates from coadsorbed nitrogen and hydrogen. In this coadsorbate structure hydrogen has to be stabilized by nitrogen, since hydrogen desorption is completed by 430 K.²⁶ Such a stabi-

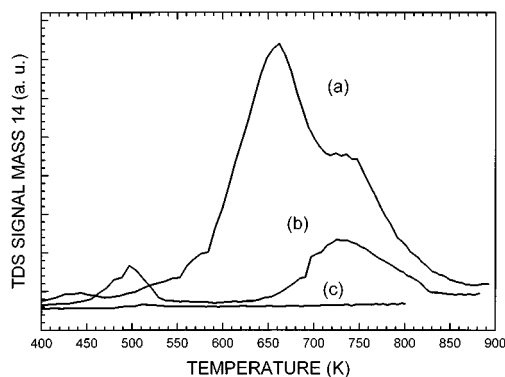


FIG. 6. TD spectra of mass 14 after dosing 3.6×10^5 L nitrogen at 450 K to Ru(1010). Spectrum (a) was taken directly after the exposure, spectrum (b) was taken 20 h later, spectrum (c) another 30 min later.

lization would be contradictory to the results of Seets *et al.*²⁷ on Ru(0001), who found that hydrogen is always destabilized in the presence of nitrogen.

C. Subsurface nitrogen

Figure 6 shows a series of TD spectra recorded after the sample was exposed to 3.6×10^5 L N₂ at 450 K. The coverage achieved in this case is higher than the coverage expected from the applied dose according to Fig. 4. This results from a different position of the sample in the chamber with respect to the ionization gauge. Spectrum (a) was recorded directly after the exposure, spectrum (b) was recorded about 20 h later, and spectrum (c) was recorded immediately after spectrum (b). The amount of desorbing nitrogen in spectrum (b) is about 15% of the amount of nitrogen desorbing in spectrum (a). The pressure in the chamber between the two TDS runs was less than 1×10^{-10} mbar. At this low pressure the adsorption of N₂ (sticking coefficient $s_0 = 1 \times 10^{-6}$) can be safely ruled out. The desorbing nitrogen in spectrum (b) can thus only originate the subsurface region. Spectrum (c) shows no further trace of nitrogen desorption. Since the nitrogen desorption is completed after two TDS runs we conclude that the nitrogen was absorbed in the subsurface region. The amount of nitrogen that desorbs from the subsurface region is thus the nitrogen of the N_α state in spectra (a) plus the nitrogen from spectra (b). The ratio between the amount of subsurface nitrogen and surface nitrogen can be estimated as 0.33.

This experiment was reproduced with a dose of 4.8×10^5 L N₂. The existence of subsurface N is further supported by the HREELS results from Fig. 2. After annealing to 630 K all nitrogen related losses have disappeared. At this temperature nitrogen from N_γ and N_β states is desorbed but not from the N_α state. The latter state corresponds to subsurface nitrogen and, therefore, does not contribute to the HREELS signal.

D. LEED

Figure 7 shows a sketch of the LEED pattern monitored after the surface was saturated with chemisorbed nitrogen. The full circles represent the Ru substrate spots, while the

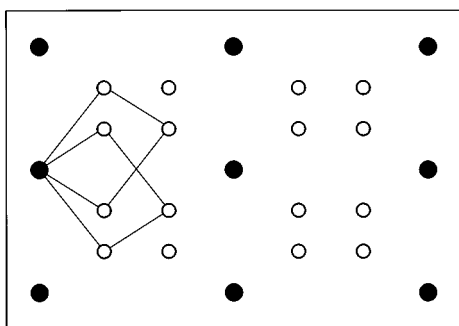


FIG. 7. Sketch of the LEED pattern monitored after the surface was saturated with nitrogen. The full circles indicate the substrate spots, while the open circles indicate the adlayer spots.

open circles represent the spots originating from the adsorbed nitrogen. The LEED pattern in Fig. 7 can be interpreted as a superposition of two domains. The unit cells of two domains are depicted by the two parallelograms in Fig. 7. The upper pattern can be described by the matrix $\begin{pmatrix} -1 & 1 \\ 2 & 1 \end{pmatrix}$. Transferring one domain of the LEED pattern into real space results in the configuration shown in Fig. 8. It is more instructive to interpret the observed pattern as a 3×3 pattern with nitrogen atoms along one diagonal of the 3×3 cell. In the other domain the nitrogen atoms occupy the other diagonal of the 3×3 cell. One domain would give rise to a coverage of $\theta_{\text{N}}=0.33$. By TDS measurements we could estimate the maximum coverage to be $\theta_{\text{N}}=0.6$. But, as shown in Sec. III C above, part of the nitrogen is absorbed in the subsurface region and therefore the amount on the surface,

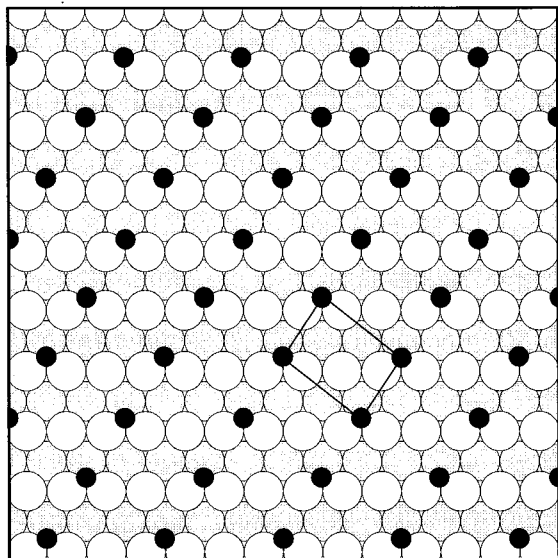


FIG. 8. A model of the distribution of the nitrogen atoms within one of the two domains on the $\text{Ru}(10\bar{1}0)$ surface inferred from the LEED pattern. The atoms in the uppermost Ru layer are represented by open circles, while the Ru layer below is shaded. The small black circles indicate the nitrogen atoms. The surface has two different threefold-hollow, fcc and hcp, sites. The nitrogen atoms are placed in the hcp site, the threefold fcc site is formed by one Ru atom in the topmost layer (unshaded) and two Ru atoms in the layer below (shaded).

which generates the LEED pattern, is less than $\theta_{\text{N}}=0.6$. If one would assume that nitrogen with a coverage of $\theta_{\text{N}}=0.6$ is adsorbed on the surface one would have to add an additional nitrogen atom in the unit cell. This is not very likely since there is no hcp threefold-hollow site in the center of the unit cell.

We have already concluded that $1/3$ of the overall amount of N is in the subsurface region so that the LEED pattern is generated through $\theta_{\text{N}}=0.4$, i.e., with about one N atom per unit cell as depicted in Fig. 8. The nominal coverage for this model is $\theta_{\text{N}}=0.33$. The surplus amount of 0.07 may be statistically distributed, increasing the background intensity but not destroying the LEED pattern.

IV. DISCUSSION

We first discuss the maximum N coverage one can achieve on the $\text{Ru}(10\bar{1}0)$ surface. To compare the coverages of nitrogen on the different surfaces the different size of the unit cells has to be taken into account. A coverage of $\theta_{\text{N}}=0.4$ on $\text{Ru}(10\bar{1}0)$ corresponds to a density of nitrogen atoms of $3.5 \times 10^{14} \text{ cm}^{-2}$. On $\text{Ru}(0001)$ a coverage of $\theta_{\text{N}}=0.25$ was achieved by ionization-gauge assisted adsorption which corresponds to a density of nitrogen atoms of $3.9 \times 10^{14} \text{ cm}^{-2}$. That means that about the same N density can be prepared by ionization-gauge assisted dissociation on both surfaces. By dissociation of ammonia, a coverage of $\theta_{\text{N}}=0.38$ was achieved on $\text{Ru}(0001)$ which gives rise to a density of $5.8 \times 10^{14} \text{ cm}^{-2}$. Higher coverages of nitrogen on $\text{Ru}(0001)$ could not be prepared since the decomposition of ammonia leads to the formation of a NH/N composite phase for which a coverage of $\theta_{\text{N}+\text{NH}}=0.47$ was found. Since the ionization-gauge assisted preparation of atomic nitrogen resulted in a coverage below the maximum nitrogen coverage on $\text{Ru}(0001)$, the same is to be expected for $\text{Ru}(10\bar{1}0)$.

We have observed two indications for subsurface nitrogen on $\text{Ru}(10\bar{1}0)$: (i) the N_α state with the highest thermal stability is fully developed only after the N_β state has been substantially populated, and (ii) additional desorption of nitrogen is observed in a second TD spectrum. The diffusion process of nitrogen from the surface into the subsurface region is quite different on $\text{Ru}(10\bar{1}0)$ and $\text{Ru}(11\bar{2}1)$. On $\text{Ru}(11\bar{2}1)$, subsurface nitrogen was monitored after exposing the surface to $6.7 \times 10^{10} \text{ L N}_2$,⁶ the TD spectrum recorded after the adsorption showed a nitrogen coverage of $\theta_{\text{N}}=0.0028$. After this TD spectrum, six TD spectra were recorded without reexposing the surface to nitrogen. The total amount of nitrogen desorbing during these seven TD spectra revealed a coverage of $\theta_{\text{N}}=0.03$ which is still only some percent of a monolayer. On $\text{Ru}(11\bar{2}1)$ the diffusion out of the subsurface region is very slow and the amount in this region is bigger than the amount of nitrogen which desorbs during the first TD spectra. On $\text{Ru}(10\bar{1}0)$ the picture is somewhat different; the subsurface region is emptied after recording the second TD spectra. The diffusion out of the subsurface region seems to proceed much faster than on $\text{Ru}(11\bar{2}1)$. The nature of the diffusion into the subsurface region is also somewhat different. While on $\text{Ru}(11\bar{2}1)$ the amount of nitro-

TABLE I. Overview of the thermal stability of the three NH_x species on three different Ru surfaces. The highest temperatures (of a short anneal) at which the NH_x species was observed are given.

	Ru(0001)	Ru(10 $\bar{1}$ 0)	Ru(11 $\bar{2}$ 1)
NH ₃	300 K (Ref. 7)	300 K	290 K (Ref. 17)
NH ₂	280 K (Ref. 12)	590 K	340 K (Ref. 17)
NH	400 K (Ref. 7)	450 K	420 K (Ref. 17)

gen buried in the subsurface region was found to be at least 10 times the amount of nitrogen on the surface, on the Ru(10 $\bar{1}$ 0) surface the amount of subsurface nitrogen is smaller than the amount of surface nitrogen. The higher amount of subsurface nitrogen on Ru(11 $\bar{2}$ 1) might be attributed to the openness of the Ru(11 $\bar{2}$ 1) surface which exposes four layers to the vacuum. On Ru(10 $\bar{1}$ 0) only two layers are exposed to the vacuum.

The HREEL spectra have been largely discussed above with the exception of the loss at 200 meV which appears after annealing the sample from 400 to 470 K. Since at this temperature only N, NH, and perhaps some H are on the surface, it is plausible that the loss is due to some N_xH_y species, most probably due to NH₂. We therefore assign the 200 meV loss to the δ (NH₂) mode. After annealing to 590 K this mode loses intensity. At the same temperature hydrogen desorbs from the H _{α} and H _{β} states. From the TD spectra of the hydrogen desorption in Fig. 5 we can estimate the NH₂ coverage to be $\theta=0.04$. This low coverage may explain why the ν_a (N–H) mode at 416 meV is not visible in Fig. 2. The thermal stability of NH₂ is higher on Ru(10 $\bar{1}$ 0) than on other Ru surfaces (see Table I). The reason for the enhanced thermal stability of NH₂ on Ru(10 $\bar{1}$ 0) is not clear yet.

The thermal stability of all NH_x species on Ru surfaces is summarized in Table I. The thermal stability of NH₃ is essentially independent of surface morphology. Even on the highly reactive Ru(11 $\bar{2}$ 1) surface ammonia is stable up to 290 K. The thermal stability of the first reaction intermediate in the hydrogenation of nitrogen, NH also shows only small variations in the thermal stability from 400 K on Ru(0001) to 450 K on Ru(10 $\bar{1}$ 0). The major difference between the three surfaces with respect to reaction intermediates can be seen in the thermal decomposition of ammonia. On Ru(0001) ammonia decomposes only if high doses are applied while the sample is above the desorption temperature of ammonia,¹¹ on Ru(11 $\bar{2}$ 1) about 25% of a monolayer of ammonia decomposes during annealing.¹⁷

V. CONCLUSIONS

We have shown that on Ru(10 $\bar{1}$ 0) atomic nitrogen can be prepared by ionization-gauge assisted adsorption. The sticking coefficient for this process is about $s_0=1 \times 10^{-6}$. The surface nitrogen species is characterized by two vibrational

modes, the vibration parallel to the surface ν_{\parallel} (Ru–N) at 41 meV and the vibration perpendicular to the surface ν_{\perp} (Ru–N) at 60 meV. If nitrogen is adsorbed at 300 K, NH₃ is synthesized from N and H. Higher sample temperatures lead to the formation of NH and NH₂. NH₂ was detected up to the surprisingly high temperature of 590 K. The TD spectra showed mainly two desorption states due to chemisorbed atomic nitrogen and nitrogen originating from the subsurface region. The activation energy for desorption from the surface is 120 ± 10 kJ/mol. At the saturation coverage of chemisorbed N ($\theta_N=0.4$) an ordered ($\begin{smallmatrix} -1 \\ 2 \\ 1 \end{smallmatrix}$) structure is formed for which a model with $\theta_N=0.33$ is proposed in which in N occupies three-fold hcp sites. At the same time an amount of N equivalent to $\theta_N=0.2$ is buried in the subsurface region.

ACKNOWLEDGMENT

We thank P. Geng for dedicated technical support.

- A. Ozaki and K. Aika, in *Catalysis-Science and Technology*, edited by J. R. Anderson and M. Boudart (Springer, Berlin, 1981), Vol. 1, p. 87.
- G. Ertl, *Catalytic Ammonia Synthesis* (Plenum, New York, 1991), p. 109.
- K.-I. Aika and K. Tamaru, *Ammonia Catalysis and Manufacture* (Springer, Berlin, 1995), p. 103.
- S. R. Tennison, *Catalytic Ammonia Synthesis* (Plenum, New York, 1991), p. 303.
- O. Hinrichsen, F. Rosowski, M. Muhler, and G. Ertl, *Chem. Eng. Sci.* **51**, 10 (1996).
- H. Dietrich, P. Geng, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **104**, 375 (1996).
- H. Shi, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **102**, 1432 (1995).
- L. Danielson, M. Dresser, E. Donaldson, and D. Sandstrom, *Surf. Sci.* **71**, 615 (1978).
- T. Matsushima, *Surf. Sci.* **197**, L287 (1988).
- K. Kunimori, M. Osumi, S. Kameoka, and S. Ito, *Catal. Lett.* **16**, 443 (1992).
- H. Dietrich, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **105**, 19 (1996).
- H. Rauscher, K. Kostov, and G. Menzel, *J. Chem. Phys.* **177**, 473 (1993).
- P. D. Reed, C. M. Comrie, and R. M. Lambert, *Surf. Sci.* **72**, 423 (1978).
- R. Ku and N. A. Gjostein, *Surf. Sci.* **64**, 465 (1977).
- E. Umbach, S. Kulkarni, P. Feulner, and D. Menzel, *Surf. Sci.* **88**, 65 (1979).
- J. Parmeter, U. Schwalke, and W. Weinberg, *J. Am. Chem. Soc.* **110**, 53 (1988).
- H. Dietrich, K. Jacobi, and G. Ertl, *Surf. Sci.* **352–354**, 138 (1996).
- H. Dietrich, K. Jacobi, and G. Ertl, *Surf. Sci.* (to be published).
- S. Schwegmann, A. P. Seitsonen, H. Dietrich, H. Bludau, H. Over, K. Jacobi, and G. Ertl, *Chem. Phys. Lett.* **264**, 680 (1997).
- H. Ibach, in *Electron Energy Loss Spectrometers—The Technology of High Performance* (Springer, Berlin, 1991).
- H. Shi, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **99**, 9248 (1993).
- H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).
- P. A. Redhead, *Vacuum* **12**, 203 (1962).
- W. Tsai and H. Weinberg, *J. Chem. Phys.* **91**, 5302 (1987).
- G. Lauth, E. Schwarz, and K. Christmann, *J. Chem. Phys.* **91**, 3729 (1989).
- G. Lauth, T. Solomun, W. Hirschwald, and K. Christmann, *Surf. Sci.* **210**, 201 (1989).
- D. C. Seets, M. C. Wheeler, and C. B. Mullins, *J. Chem. Phys.* **103**, 10399 (1995).