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Adsorption and thermal dehydrogenation of ammonia on Ru(11 $\bar{2}$ 1)

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Adsorption and thermal dehydrogenation of NH₃, adsorbed at 80 K on the open Ru(11 $\bar{2}$ 1) surface, was studied using high-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). For the NH₃ monolayer, a strong dipole-active mode is found at 15 meV which is newly assigned to T_z , the frustrated-translation mode perpendicular to the surface of NH₃ bonding with the nitrogen atom to the Ru surface. Increasing the temperature, 70% of NH₃ desorbs before a channel for dehydrogenation opens at about 280 K. The remaining 30% decomposes completely during further warming to 470 K. The dehydrogenation of NH₃ gives rise to four peaks in the H₂ TDS which are assigned to desorption of coadsorbed hydrogen at 220 K and three dehydrogenation reaction steps at 320, 360, and 420 K in accordance with HREELS. The reaction intermediates NH₂ and NH are identified through HREELS. In a new interpretation NH₂ is characterized by intense modes at 163 meV (rocking) and at 189 meV (scissoring). Using a maximum entropy algorithm six frequencies for $\nu(\text{Ru-N})$ were resolved at 46, 50, 58, 61, 69, and 75 meV. © 2001 American Institute of Physics. [DOI: 10.1063/1.1390523]

I. INTRODUCTION

Ru-based catalysts may become the second-generation industrial catalysts for NH₃ synthesis¹ which, according to general belief, proceeds via stepwise recombination of chemisorbed atomic nitrogen and hydrogen as it was found for iron-based catalysts earlier.² Thus, one expects NH and NH₂ to occur as reaction intermediates. Not very much was known about these species, their preparation, and spectroscopic characterization, till now.

Early experiments on the adsorption of NH₃ on Ru(0001) have been carried out by Danielson *et al.*^{3,4} NH₃ desorbs reversibly for adsorption temperatures below 300 K and the desorption is completed at about 350 K. Two different desorption states are distinguished in the monolayer regime.⁵ Dissociation of NH₃ on Ru(0001) has been achieved by electron bombardment⁴ or by exposing the surface to large fluences of NH₃ for surface temperatures maintained above 300 K.^{6,7} The vibrational frequencies for mono-, second-, and multi-layer NH₃ on Ru(0001) have been profoundly reviewed by Parmeter *et al.*⁸ which have suggested that NH₃ adsorbs at an on-top site.

Upon heating, dehydrogenation of NH₃ has been observed on a stepped Ru(1,1,10) surface by Egawa *et al.*⁷ From x-ray photoelectron spectroscopy (XPS) they concluded that NH_x ($x=1, 2$) is formed after heating to 300 K. A high density of NH_x species could be detected only under flow conditions at 380 K.⁷ Decomposition of N₂H₄ on Ru(0001) resulted in rather complex vibration spectra in high-resolution energy-loss spectroscopy (HREELS) from which fingerprints for NH and NH₂ were derived.⁹ For Ni(110), held at 344 K in an ambient pressure of 2×10^{-8} mbar NH₃, a mode at 188 meV was assigned to the NH₂ scissoring mode.¹⁰ The analysis was hampered, how-

ever, through co-adsorbed NH₃ and CO. Synthesis of NH₃ from adsorbed N and H has been studied by Shi *et al.*¹¹

Recently, we have shown that Ru(11 $\bar{2}$ 1) (see Fig. 1) is suited to study the dehydrogenation of NH₃ giving rise to NH and NH₂, the expected decomposition products.¹² Our analysis was based on the assumption that NH is characterized by a NH bending mode of high energy (165 meV, 1350 cm⁻¹) on Ru surfaces.⁹⁻¹¹ In a more recent study Stauffer *et al.*,¹³ have performed calculations of NH on a variety of different small Ru clusters of 4–7 Ru atoms using density-functional theory. NH was found to be energetically favored on a threefold-hollow site at perpendicular orientation. With respect to our analysis, the most important point is their finding that the bending mode frequencies lie below about 100 meV for all models. The conclusion was that any imaginable error in the calculations could never lead to a frequency as high as 165 meV. Therefore, conclusions based on the according assignment in Refs. 9–11 have to be revised in the future.

In this contribution we discuss the vibrational spectra of ammonia and newly assign the frustrated-translation mode perpendicular to the surface. Also, we present the data on NH₃ dehydrogenation in greater detail than before and revise our recent assignment¹² of the NH and NH₂ intermediates resulting in a more consistent interpretation.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum apparatus with a base pressure of 3×10^{-11} mbar which was achieved by a pumping line consisting of a Ti-sublimation pump, a turbo-molecular pump with magnetic suspension (Leybold, NT340M), a drag pump (Balzers, TCP015), and a diaphragm pump. The apparatus consisted of two chambers—the upper chamber contained an argon ion gun, a quadrupole mass spectrometer, and a low-energy elec-

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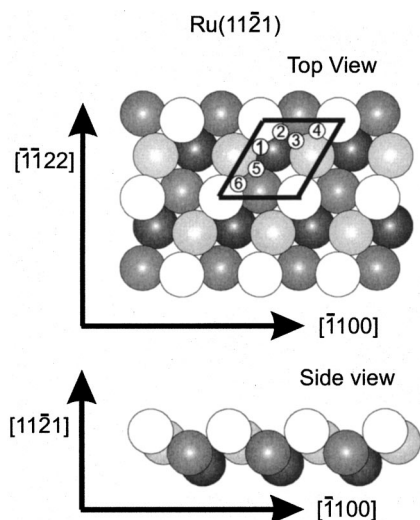


FIG. 1. Top view and side view of the unrelaxed Ru(11 $\bar{2}$ 1) surface including the four topmost layers. The top layer is light, the layers below are indicated more dark with increasing depth.

tron diffraction (LEED) optics,—the lower chamber housed an Ibach-type HREEL spectrometer¹⁴ for recording vibrational spectra. The two chambers 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. HREEL spectra were taken at an angle of incidence of 60° with respect to the surface normal in specular geometry. The primary energy was 2.5 eV and the energy resolution was set to 3.8 meV.

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 only molecules desorbing from the sample surface. The signal for e/m ratios of 2, 14, 17, and 28, were recorded quasi-simultaneously to follow the desorption of H_2 , N_2 , NH_3 , and CO. The cracking pattern of N_2 and CO differ at mass 14 and, therefore, allow to distinguish between CO and N_2 desorption.

The Ru(11 $\bar{2}$ 1) sample was clamped at two edges between two tungsten wires and heated by electron bombardment from the back side. The crystal temperature was measured by a Ni–Cr/Ni thermocouple spot welded on the upper edges of the sample. Cleaning of the surface was achieved by repeated cycles of sputtering and annealing at 1560 K. The cleanliness of the surface was verified by LEED and HREELS. The surface exhibited a sharp 1×1 pattern in LEED. The exposure is given in units of Langmuir (1 Langmuir = 1.33×10^{-6} mbar s). Absolute coverage could only be estimated by comparison with Ru(0001) since no coverage reference exists for Ru(11 $\bar{2}$ 1) up to now. The identification of adsorbates by HREELS is a rather difficult task on Ru(11 $\bar{2}$ 1). These difficulties arise from the high reactivity and the sparse information on the vibrational modes on this surface. A contamination like CO give rise to many different vibrational losses which are in part due to CO dissociation, similarly as observed for Ru(11 $\bar{2}$ 0).¹⁵

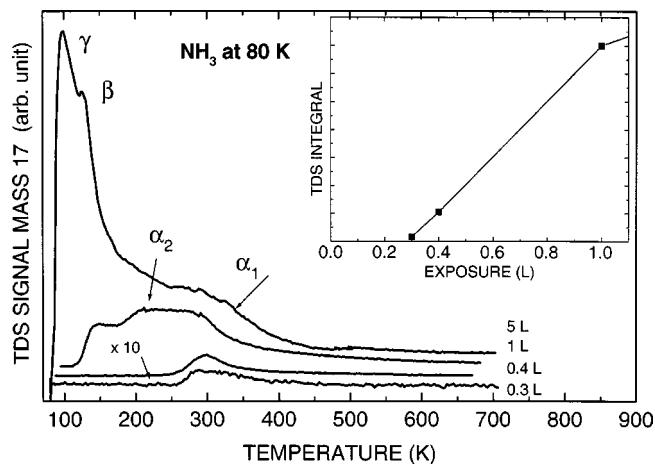


FIG. 2. TD spectra of NH_3 (mass 17) for a sequence of NH_3 exposures on Ru(11 $\bar{2}$ 1) at 80 K. The inset shows the integrated TDS intensity vs exposure.

III. RESULTS

A. TDS of ammonia and its dehydrogenation products

In Fig. 2 TD spectra of NH_3 are shown for different exposures at 80 K. After an exposure of 0.3 L NH_3 , only a very small desorption peak occurs at about 300 K. (Note that this spectrum is scaled up by a factor of 10.) Increasing the exposure to 0.4 L, the desorption peak at 300 K substantially gains intensity indicating that NH_3 starts desorbing. As we will demonstrate by HREELS below, the first 0.3 L of NH_3 dissociate. At an exposure of 1 L the α state is completely filled and the β state starts emerging at about 140 K. After exposing the surface to 5 L NH_3 , the β state is fully developed with a peak at 125 K, and the γ state appears at 100 K. Using a frequency factor of $\nu = 10^{13} \text{ s}^{-1}$, the activation energies for the desorption from the β state ($E_d = 30 \text{ kJ/mol}$) and from the γ state ($E_d = 25 \text{ kJ/mol}$) can be calculated. Due to its strong broadening we cannot derive an activation energy for the α state. The TD spectra from Ru(11 $\bar{2}$ 1) are quite similar to the TD spectra of NH_3 from Ru(0001).⁵ Therefore, we attribute the β state to the desorption of second-layer ammonia and the γ state to the desorption of multilayer ammonia. On Ru(0001) Benndorf *et al.*⁵ distinguished between two α states, which may also be recognized from our spectra (denoted as α_1 and α_2).

In order to follow the decomposition in more detail, we have studied TD spectra of the products hydrogen and nitrogen simultaneously. Figure 3 exhibits—together in the same figure—the TD spectra of mass 2 for H_2 and mass 14 for N_2 for several exposures of NH_3 at 80 K. Mass 14 was chosen in order to differentiate between CO and N_2 . At an exposure of 0.04 L, the TD spectrum of mass 2 exhibits a broad peak at 340 K. From its size and the according HREEL spectra¹⁶ we conclude that it is mainly due to hydrogen adsorbed from the residual gas which cannot be avoided for this reactive Ru surface even at a background pressure of 3×10^{-11} mbar. The H_2 spectra, taken after exposing the sample to 0.3 L NH_3 , can be divided into the following four parts: α - H_2 (420 K), β - H_2 (360 K), γ - H_2 (320 K), and δ - H_2 (220 K).

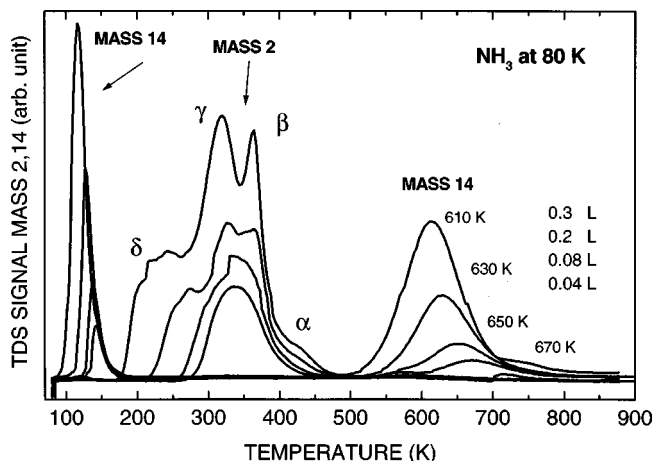


FIG. 3. TD spectra for a sequence of NH_3 exposures on $\text{Ru}(11\bar{2}1)$ at 80 K. The pressure increase for N_2 (mass 14) and H_2 (mass 2) was recorded simultaneously. Parameter is the NH_3 exposure in units of Langmuir (1 L=1.33 mbar \times s).

If one increases the exposure of NH_3 , only the TD spectrum of mass 17 changes (see Fig. 2), while the spectra of mass 2 and mass 14 remain unchanged, i.e., larger amounts of NH_3 do not dissociate.

As indicated by the TD spectra of mass 14 in Fig. 3, the adsorption of molecular nitrogen is observed below 140 K. This molecular nitrogen is most likely due to decomposition of NH_3 in the dosing line. Between 670 and 610 K, N_2 is observed associatively desorbing in a second-order process. Compared to $\text{Ru}(0001)$ ¹⁷ and $\text{Ru}(10\bar{1}0)$ ¹⁸ the thermal stabilization of N is smaller on $\text{Ru}(11\bar{2}1)$, i.e., N_2 desorbs at a lower temperature.

In order to examine whether the H_2 TD spectra of Fig. 3 are typical for H_2 desorption from a H-covered $\text{Ru}(11\bar{2}1)$ surface, we performed TDS experiments after dosing H_2 which are discussed elsewhere.¹⁶ From this study we show in Fig. 4 one H_2 TD spectrum after an exposure of 0.8 L H_2 at 80 K, and compare it with the H_2 TD spectrum following a 0.3 L NH_3 exposure at 80 K. Note that the intensities in Fig.

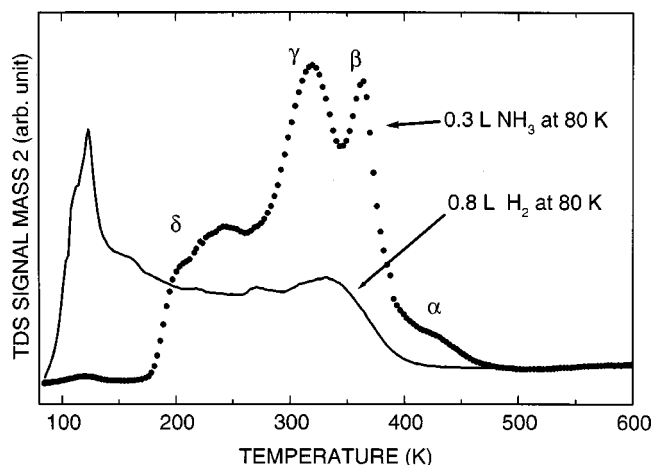


FIG. 4. TD spectra for 0.8 L H_2 on $\text{Ru}(11\bar{2}1)$ at 80 K (full curve). For comparison the TD spectrum of mass 2 for an exposure 0.3 L NH_3 at 80 K is shown. Note that the intensities are scaled.

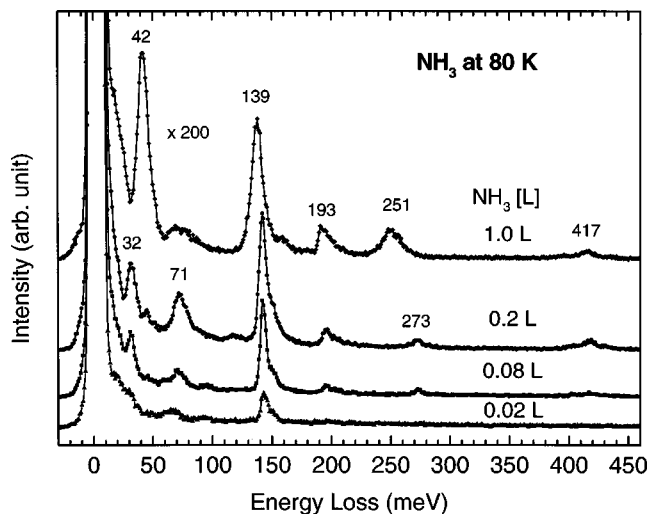


FIG. 5. HREEL spectra for a sequence of NH_3 exposures on $\text{Ru}(11\bar{2}1)$ at 80 K. The primary energy of the electrons was 2.5 eV. All spectra were recorded in specular geometry with an angle of incidence of 60° with respect to the surface normal. Parameter is the NH_3 exposure in units of Langmuir (L).

4 are scaled. A comparison of the H_2 TDS integrals leads to the following result: From a NH_3 exposure of 0.3 L, which carries a H_2 equivalent of 0.45 L H_2 , about three times more H_2 desorbs than from chemisorbed hydrogen in the same temperature interval. Therefore, we conclude that the H_2 signals in Fig. 3 are mainly due to NH_3 decomposition. With the help of HREELS we will demonstrate in the following that three out of the four hydrogen states are due to dehydrogenation of NH_3 rather than to adsorption of atomic hydrogen.

B. HREELS of ammonia

HREEL spectra following NH_3 adsorption at 80 K (Fig. 5) exhibit the evolution of the typical vibrations of chemisorbed NH_3 as assigned and summarized in Table I. Most indicative for NH_3 is the umbrella mode at around 140 meV. Co-adsorbed N_2 is observed with losses at 273 meV for the internal stretch mode $\nu(\text{N-N})$, and at 32 meV for the external stretch mode of N_2 against the surface $\nu(\text{Ru-N}_2)$. For exposures larger than 0.4 L, $\nu(\text{N-N})$ shifts to 250 meV and $\nu(\text{Ru-N}_2)$ to 42 meV due to interaction with NH_3 . The vibrational features for the monolayer saturate at 1 L. The vibrational energies, found for the NH_3 multilayer after an exposure of 5 L NH_3 , are in good agreement with data from the literature⁸ and will not be discussed here. When the NH_3 monolayer builds-up, the umbrella mode $\delta(\text{NH}_3)$ softens with coverage as shown in Fig. 6. This effect was shown to be due to a Stark shift in the electric field of the static NH_3 dipoles within the adlayer on a $\text{Ru}(0001)$ surface.¹⁹

After dosing NH_3 at 180 K (see the lowest spectrum in Fig. 7) the spectra are better resolved than after dosing at 80 K (Fig. 5). The N_2 losses are no longer observed since chemisorbed N_2 is not stable at this temperature. The strong N_2 peak at 42 meV in Fig. 5 has vanished and only a weak peak at 44 meV is left. This loss is probably due to a librational mode since at this energy such a mode has been observed for thicker layers on $\text{Ru}(0001)$.⁸ At 15.5 meV, well

TABLE I. Vibrational energies in units of meV for NH_x ($x=0\cdots 3$) on Ru(11 $\bar{2}$ 1) compared to data from the literature for Ru(0001) (Ref. 8). Variation of energy with coverage is indicated by a dash with the coverage increasing from left to right. The vibrational modes are denominated as T (translational mode); ω (wagging mode); ρ (rocking mode); δ (bending or scissoring mode); ν (stretching mode). s , symmetric; a , asymmetric.

	Ru(0001) Ref. 8 NH_3	Ru(11 $\bar{2}$ 1) This work NH_3	Ru(11 $\bar{2}$ 1) This work NH_2	Ru(11 $\bar{2}$ 1) This work NH	Ru(11 $\bar{2}$ 1) This work N
T_z	...	15	64	84	46, 50, 58, 61, 69, 75
$\omega(\text{NH}_x)$	42 ^a	44			
$\rho(\text{NH}_x)$	78	66–74	163	89	...
$\delta_s(\text{NH}_x)$	143–133	143–133	189
$\delta_a(\text{NH}_x)$	197	194
$\nu_s(\text{N-H})$	407	400	408	410	...
$\nu_a(\text{N-H})$	421	420	419

^aThis mode was assigned to T_z by Parmeter *et al.* (Ref. 9).

separated from the elastic peak, a strong peak has developed. Since the intensity of this low-energy mode varies with coverage similarly as the other NH_3 modes, we assign it to T_z , the frustrated translation perpendicular to the surface. With decreasing θ_{NH_3} , T_z shifts from 15.5 to 11 meV (at 290 K).

There is another new loss at 157 meV which cannot be attributed to a known vibration. A detailed analysis of the HREEL spectra of atomic hydrogen in Ref. 16 shows that it is not due to H. From its appearance together with T_z one may think that it is due to a combination loss of $\delta_s(\text{NH}_3)$ at 137.7 meV and T_z . The problem, however, arises that the energy is higher by 3.8 meV compared to the simple sum of energies whereas one expects a smaller value due to anharmonicity. Also the intensity is too high. Therefore, we abandon this interpretation. Another possibility may be that a second, differently bonded NH_3 species occurs. A similar observation was made for Ru(0001) recently.¹⁹ We cannot give a final answer here which we, however, do not consider as important since this weak peak does not influence our conclusions.

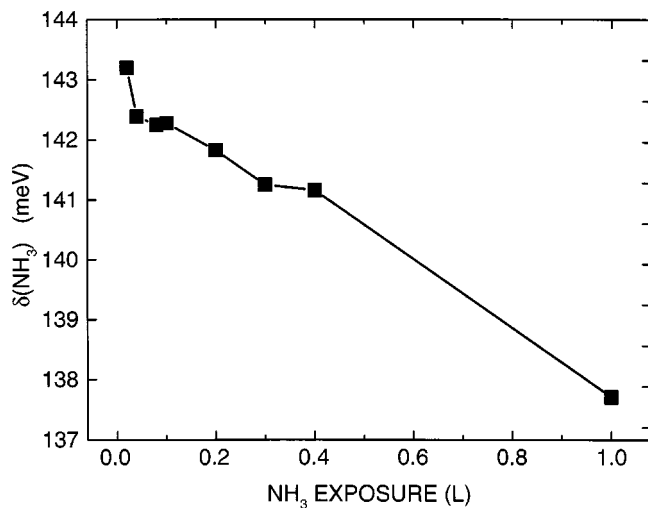


FIG. 6. The vibrational energies of the umbrella mode $\delta(\text{NH}_3)$ vs exposure.

C. Thermal dehydrogenation of NH_3 probed by HREELS

In order to examine the thermal dehydrogenation of NH_3 , 1 L NH_3 was exposed at 180 K. The respective HREEL spectra are shown in Fig. 7. After heating to 250 K, all NH_3 losses lose some intensity. The umbrella mode shifts to 140.4 meV and loses about 20% in intensity. The temperature region between 180 and 250 K is characterized in TDS through the $\delta\text{-H}_2$ state and the $\alpha_2\text{-NH}_3$ state.

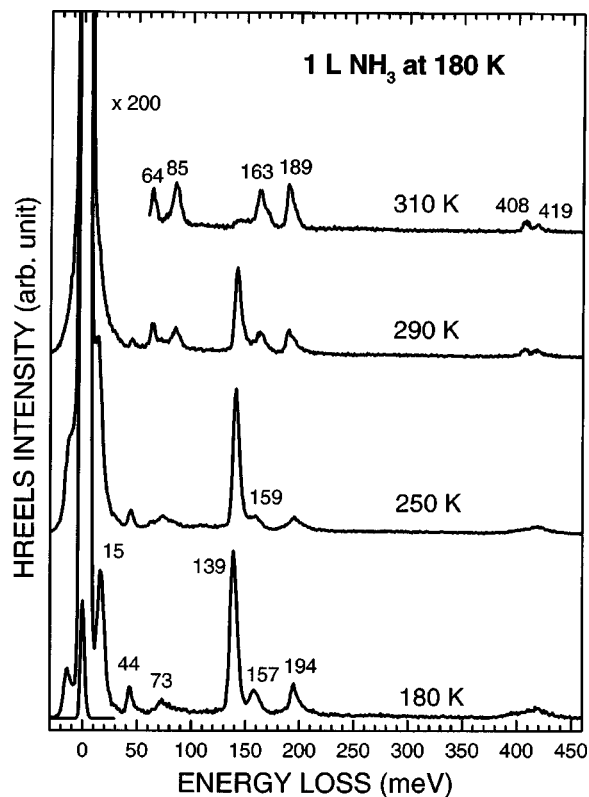


FIG. 7. HREEL spectra for an exposure of 1 L NH_3 on Ru(11 $\bar{2}$ 1) at 180 K. After exposure the sample was subsequently annealed to the indicated temperatures. The primary energy of the electrons was 2.5 eV. All spectra were recorded in specular geometry with an angle of incidence of 60° with respect to the surface normal.

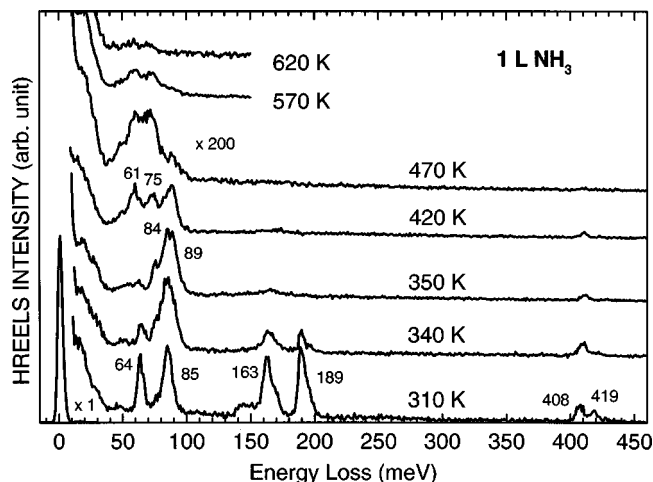


FIG. 8. HREEL spectra for an exposure of 1 L NH₃ at 180 K. After exposure, the sample was subsequently annealed to the indicated temperatures. For the spectra recorded for 470 K and higher temperatures, the sample was exposed to 1 L NH₃ at 320 K. The primary energy of the electrons was 2.5 eV. All spectra were recorded in specular geometry with an angle of incidence of 60° with respect to the surface normal.

Heating to 310 K lets the NH₃ modes disappear and reveals new features at 64, 85, 163, and 189 meV. According to the calculation of Staufer *et al.*¹³ the mode at 163 meV cannot be assigned to the NH bending mode as this mode has to be lower than 100 meV in energy. Therefore, the mode at 163 meV can only be due to NH₂. This assignment is new and differs from that in our recent contribution.¹² Besides NH₂, also some amount of NH is found as demonstrated by its bending mode at 85 meV. So, the new assignment does not change our old assignment of the γ -H₂ state as due to the



and



reactions. The separation of NH and NH₂ is better achieved for Ru(11 $\bar{2}$ 0)²⁰ and supports the assignment given here.

After desorption of NH₃, the $\nu(\text{N-H})$ region is more structured exhibiting two rather sharp losses at 408 and 419 meV due to the symmetric and asymmetric N-H stretching modes of NH₂. This temperature region is characterized by γ -H₂ as well as by α_1 -NH₃. Thus, after heating to 310 K, NH₃ has disappeared completely, being either desorbed or dehydrogenated to NH₂ or NH.

Figure 8 exhibits HREEL spectra for further annealing to higher temperatures. The spectra at 310 K in Figs. 7 and 8 are from the same data set. By heating to 350 K the peaks at 64, 163, 189, and 419 meV disappear which indicates that NH₂ is not present at the surface anymore. Besides the low-lying modes, there are four modes left at 74, 84, 89, and 412 meV for NH. The existence of NH on the surface is proven by the $\nu(\text{N-H})$ loss at 412 meV and the α -H₂ state at 420 K in TDS which was assigned to dehydrogenation of NH. The peak at 74 meV is probably due to N. The peaks at 84 and 89

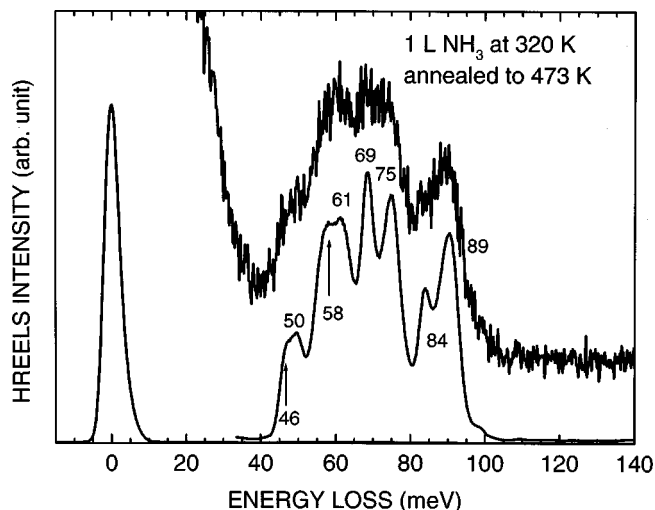


FIG. 9. HREEL spectra for 1 L NH₃ exposed to Ru(11 $\bar{2}$ 1) at 320 K and subsequent annealing to 470 K. The noisy line is the measured spectrum while the solid line between 30 and 100 meV represents the result of a deconvolution for which the details are given in the text.

meV are assigned to the stretching and bending modes of NH.

From the TD spectra shown in Fig. 4, it is found that at about 390 K the main amount of hydrogen has desorbed from the surface and only the weakly bonded α -H₂ state is left which is identified as due to the decomposition of NH by HREELS. By heating the sample to 420 K, the losses attributed to NH at 84 and 89 meV decrease in intensity. The losses at 61 and 75 meV gain intensity and are attributed to $\nu(\text{Ru-N})$ modes of N. By further heating to 470 K, the NH-related losses vanish nearly completely, and the $\nu(\text{Ru-N})$ losses form a band between 50 and 75 meV. To study this band in detail we have used a maximum-entropy deconvolution algorithm.²¹ The results are presented in the following section. At higher temperatures nitrogen desorbs from the surface which is completed at 620 K. The Ru(11 $\bar{2}$ 1) phonon at 20 meV reappears. A summary of the vibrational frequencies of NH_x is given in Table I.

D. Deconvolution of the $\nu(\text{Ru-N})$ modes

To derive more information about the vibrational frequencies of the $\nu(\text{Ru-NH})$ and $\nu(\text{Ru-N})$ modes a maximum-entropy algorithm²¹ was used. This algorithm does not require any fit parameter and combines maximum-likelihood and maximum-entropy methods in a Bayesian framework. Figure 9 shows the HREEL spectrum following a 1 L NH₃ exposure at 320 K and annealing to 470 K and the spectrum after deconvolution by the maximum-entropy algorithm. The deconvoluted spectrum clearly resolves the two NH related losses at 84 and 89 meV. The broad band of N related losses gets resolved into six losses at 46, 50, 58, 61, 69, and 75 meV. The deconvolution of other spectra for lower annealing temperatures shows the same loss energies of the main peaks but different intensities. The variety of $\nu(\text{Ru-N})$ related losses may be correlated with the variety of possible adsorption sites on the Ru(11 $\bar{2}$ 1) surface as indicated in Fig. 1.

IV. DISCUSSION

The TD spectra of second- and multilayer NH₃ on Ru(11 $\bar{2}$ 1) differ only slightly from the respective TD spectra of NH₃ on Ru(0001). The desorption temperatures are about 15 K lower which is within the limit of accuracy of absolute temperature calibration at surfaces.

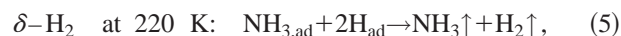
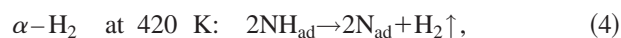
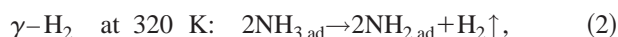
The coverage of the NH₃ monolayer can only be estimated since a LEED pattern of a NH₃-derived superstructure is not observed and there are no easily reproducible nitrogen standards available in surface physics. On Ru(0001), a NH₃ monolayer is formed by dosing 1 L NH₃⁸ and a coverage of $\theta_{\text{NH}_3} = 0.25$ is estimated in accordance with the 2 \times 2 LEED pattern. Assuming the same sticking coefficient for NH₃ on Ru(11 $\bar{2}$ 1), an exposure of 1 L would formally result in a coverage of $\theta_{\text{NH}_3} = 0.89$. The different coverage for the same dose and sticking coefficient arises from the different atom densities in the uppermost layer for Ru(0001) ($15.7 \times 10^{14} \text{ cm}^{-2}$) and Ru(11 $\bar{2}$ 1) ($4.7 \times 10^{14} \text{ cm}^{-2}$). Given the physical size of NH₃ (lateral diameter for an upright NH₃ $\approx 3.6 \text{ \AA}$) and the length of the vector of the Ru(11 $\bar{2}$ 1) 1 \times 1 unit cell of 4.69 \AA , it is very likely that a coverage of $\theta_{\text{NH}_3} = 1.0$ is reached following an exposure of 1 L at 180 K. At this coverage, NH₃ has still ample space to freely rotate and bend around its adsorption site.

HREELS demonstrates that NH₃ does not dissociate on Ru(11 $\bar{2}$ 1) for adsorption temperatures $\leq 180 \text{ K}$, but adsorbs molecularly and builds-up mono- and multilayers as known for Ru(0001). For the NH₃ monolayer, the vibrational spectra, known from the Ru(0001) surface⁸ (see Table I), are reproduced. Only, a translation mode T_z at 15.5 meV is newly resolved. As this loss is very intensive and dipole active, we assign it to the frustrated translation perpendicular to the surface. This new interpretation was recently introduced by Widdra *et al.*¹⁹ for Ru(0001) although in their spectra this mode was ten times weaker than the umbrella mode. In our case, T_z is of the same intensity as the umbrella mode making our assignment even more convincing. This mode was not observed by Parmeter *et al.*⁸ due to the limited energy resolution at that time. Their assignment of a weak mode at 42 meV as due to T_z is not correct according to our and Widdra's experiments. We have not included this value, therefore, in Table I. Interestingly, Parmeter *et al.* observed the mode at 42 meV only in off-specular direction which fits well to our assignment of this mode to a librational (wagging) mode.

During growth of the monolayer at 80 K (see Fig. 5), T_z is not observed due to lacking energy resolution, co-adsorption of N₂ and H₂, and probably some disorder in the adlayer. After heating to 180 K (see Fig. 7) these problems seem to be solved and the spectrum becomes better resolved. After annealing to 250 K the NH₃ spectrum is not changed; T_z is shifted from 15.5 to 11.2 meV and δ_s from 139 to 142 meV. Both effects are due to a change in coverage and may be identified as due to dipole-dipole interaction in case of T_z and Stark effect in case of δ_s . Two monolayer states which may be inferred from TDS are not disclosed by HREELS, so that the split into the α_1 and α_2 states is assigned to repulsive lateral interaction.

Following an exposure of 0.3 L, NH₃ is fully dissociated upon heating. From TDS we derived that the sticking coefficient of NH₃ is constant for an exposure between 0.3 and 1 L. It is reasonable to assume that this holds also for an exposure below 0.3 L. Therefore, we assume $\theta_{\text{NH}_3} = 0.3$ for an exposure of 0.3 L, i.e., one molecule in about every third 1 \times 1 unit cell. For an exposure $\leq 0.3 \text{ L}$, only dissociation and for an exposure $> 0.3 \text{ L}$ dissociation and desorption are observed in parallel if one raises the sample temperature. How much NH₃ is decomposed is a question of the two competing channels of desorption and dehydrogenation rather than of a vanishing reactivity of the surface at a given (rather small) coverage of dehydrogenation products.

For NH₃ dehydrogenation two reaction intermediates are expected namely NH and NH₂. We have observed the following four steps of the dehydrogenation which manifest themselves in H₂ desorption states (α -H₂ to δ -H₂) and in HREELS:



The separation of these states is not complete, since we observe from both, TDS and HREELS, that at the γ -H₂ release, NH₂ and also NH is formed and at the β -H₂ release NH and also N is formed. The amount of released H₂ decreases from the γ - to the β - to the α -state. The barrier for NH₃ desorption decreases with coverage. For the full monolayer the barrier for desorption is lower than that for dehydrogenation. When the dehydrogenation begins at 280 K an estimated amount of about 2/3 of the NH₃ monolayer is desorbed already. This is the more fortuitous reason of why only about 1/3 of a NH₃ monolayer is decomposed.

The hydrogen TD spectra during dehydrogenation of NH₃ give some insight into the dehydrogenation reaction. At an exposure of 0.3 L the four desorption states are fully developed. For the lowest NH₃ exposure (0.04 L) a surprisingly strong H₂ desorption is observed. This is mainly due to H₂ adsorbed from the residual gas before and during exposure of NH₃ which cannot be avoided for this reactive Ru surface even at a background pressure of $3 \times 10^{-11} \text{ mbar}$. This hydrogen desorbs together with NH₃. The desorption temperature of 220 K is smaller than that found for first 0.3 monolayer of hydrogen on the bare surface. Thus, NH₃ destabilizes coadsorbed hydrogen. This is similar to N+H coadsorption on Ru(0001); for fractions of 0.26–0.37 of a N monolayer, some part of the hydrogen is strongly destabilized.²² At a first look the size of the hydrogen signal in Fig. 4 is surprisingly large. It is understood, however, considering that at those temperatures, for which the dehydrogenation begins, NH₃ as well as hydrogen is already largely destabilized. Therefore, most of the hydrogen, split off the NH_x, desorbs immediately. The dehydrogenation of 0.3 ML of NH₃ produces 0.3 ML of N and 0.9 ML of H, of which the latter one desorbs immediately.

TABLE II. Vibrational energies in units of meV for NH_2X , X as indicated. The vibrational modes are denominated as T (translational mode); τ (twisting mode); ω (wagging mode); ρ (rocking mode); δ (bending mode); ν (stretching mode). s , symmetric; a , asymmetric.

	NH_2CHO gas phase (Ref. 23)	NH_2CO on Ru(0001) (Ref. 24)	NH_2 on Ru($\bar{1}\bar{1}\bar{1}$) this work
T_z	64
τ	36
ω	75	103	...
ρ	131	^a	163
δ	194	^a	189
$\nu_a(\text{N-H})$	439	417 ^b	419
$\nu_s(\text{N-H})$	428	417 ^b	408

^a4 peaks are found at 196, 170, 161, and 126 meV due to $\nu_s(\text{NCO})$, $\nu_a(\text{NCO})$, $\delta(\text{NH}_2)$, and $\rho(\text{NH}_2)$ without specific mode assignments.

^b ν_s , ν_a not resolved.

The reaction intermediate NH_2 is found on Ru($\bar{1}\bar{1}\bar{1}$) in a temperature range between 290 and 340 K. Initiated by the calculations of Staufer *et al.*,¹³ we newly assign the NH_2 modes (see Table II). Our assignment is supported by vibrational data from gas phase²³ and adsorbed²⁴ formamide (NH_2CHO) which contains an end-standing NH_2 Group. Whereas the identification of the NH_2 group from the stretching and bending modes is quite convincing, the assignment of the librational (rocking, wagging, twisting) modes is still not quite obvious. However, if one believes that, during adsorption, the wagging mode ω shifts from 75 (gas phase) to 103 meV [for NH_2CO on Ru(0001), see Table II], one also may believe in a shift of the rocking mode energy from its gas phase value of 131 to a value of 163 meV for the NH_2 intermediate in our case.

The energy barriers for the processes (2)–(4) continuously increase. Assuming first-order reactions and a prefactor of 10^{13} per s leads to an activation barriers of 88 kJ/mol for reaction (2), 100 kJ/mol for (3), and 117 kJ/mol for (4). This is the reason of why we can observe all reaction intermediates mainly sequentially. On Ru(0001) and also in microkinetic modeling of gas flow experiments²⁵ the barrier for (3) is smaller than for (2) and NH_2 can not be stabilized in NH_3 dehydrogenation. The amount of released hydrogen decreases gradually from the γ - to the β - and to the α -state. This can be understood by assuming that in each dehydrogenation step some of the reactants proceed immediately further to the following step.

The N coverage can be derived from the NH_3 coverage. Since an ammonia coverage of $\theta_{\text{NH}_3}=0.3$ fully dissociates, the coverage of nitrogen is also $\theta_{\text{N}}=0.3$. Compared to the maximum nitrogen coverage of $\theta_{\text{N}}=0.47$ achieved on Ru(0001),²⁶ this coverage is relatively small keeping in mind the different sizes of the unit cells. It is surprising that six slightly different $\nu(\text{Ru-N})$ stretch frequencies are observed although θ_{N} is rather small. We conclude that the adsorption energies at the different sites within the 1×1 unit cell are not very different. Therefore, the entropy term in the free enthalpy of adsorption may prevent an ordering within the adlayer. Instead from unit cell to unit cell, N occupies different sites. First attempts to increase θ_{N} through NH_3 decomposi-

tion failed. The number of six different $\nu(\text{Ru-N})$ frequencies nicely correlates with six different threefold-hollow sites in the unit cell (see Fig. 1).

V. CONCLUSION

At 80 K NH_3 adsorbs in mono- and multilayers on Ru($\bar{1}\bar{1}\bar{1}$). The observed vibrations are essentially identical to those found for Ru(0001). For the monolayer we newly assign the perpendicular translation mode T_z at 11.2–15 meV. This assignment is in agreement with that given recently for Ru(0001).¹⁹ Whereas in TDS two monolayer states are observed, there is no indication of two different states found in the HREEL spectra.

The Ru($\bar{1}\bar{1}\bar{1}$) surface is more reactive than Ru(0001). After adsorption at temperatures ≤ 180 K, an amount of 0.3 monolayer of NH_3 decomposes completely into N and H during annealing to 470 K. That only a fraction x of a monolayer is decomposed, is simply due to the fact that dehydrogenation starts only at about 280 K, at which temperature about a $1-x$ fraction of a monolayer is already desorbed. At higher coverage, desorption and dehydrogenation occur one after the other and the dehydrogenation part does not increase.

The reaction intermediates NH_2 and NH were identified using HREELS. The new assignment of the NH_2 modes is based on a recent calculation.¹³ Interestingly, on Ru($\bar{1}\bar{1}\bar{1}$) the activation barrier for hydrogen abstraction from NH_x increase stepwise when x decreases. This made it possible to identify the dehydrogenation steps.

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- S. R. Tennison, in *Catalytic Ammonia Synthesis*, edited by J. R. Jennings (Plenum, New York, 1991), p. 303; K. Aika, *Angew. Chem. Int. Ed. Engl.* **25**, 558 (1986).
- G. Ertl, in *Catalytic Ammonia Synthesis*, edited by J. R. Jennings (Plenum, New York, 1991), p. 109.
- L. R. Danielson, M. J. Dresser, E. E. Donaldson, and J. T. Dickinson, *Surf. Sci.* **71**, 599 (1978).
- L. R. Danielson, M. J. Dresser, E. E. Donaldson, and D. T. Sandstrom, *Surf. Sci.* **71**, 615 (1978).
- C. Benndorf and T. Madey, *Surf. Sci.* **135**, 164 (1983).
- W. Tsai and W. H. Weinberg, *J. Phys. Chem.* **91**, 5302 (1987).
- C. Egawa, S. Naito, and K. Tamaru, *Surf. Sci.* **138**, 279 (1984).
- J. E. Parmeter, Y. Wang, C. B. Mullins, and W. H. Weinberg, *J. Chem. Phys.* **88**, 5225 (1988).
- H. Rauscher, K. L. Kostov, and D. Menzel, *Chem. Phys.* **177**, 473 (1993).
- I. Bassignana, K. Wangmann, J. K ppers, and G. Ertl, *Surf. Sci.* **175**, 22 (1986).
- H. Shi, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **102**, 1432 (1995).
- H. Dietrich, K. Jacobi, and G. Ertl, *Surf. Sci.* **352–354**, 138 (1996).
- M. Staufer, K. M. Neyman, P. Jakob, V. A. Nasluzov, D. Menzel, and N. R sch, *Surf. Sci.* **369**, 300 (1996).
- H. Ibach, *Electron Energy Loss Spectroscopy—The Technology of High Performance* (Springer, New York, 1991).
- J. Wang, Y. Wang, and K. Jacobi, *Surf. Sci.* (to be published).
- C. Y. Fan and K. Jacobi, *Surf. Sci.* **21**, 482 (2001).

- ¹⁷H. Shi, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **99**, 9248 (1993).
- ¹⁸H. Dietrich, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **106**, 9313 (1997).
- ¹⁹W. Widdra, T. Moritz, K. L. Kostov, P. König, M. Staufer, and U. Birkenheuer, *Surf. Sci.* **430**, L558 (1999).
- ²⁰Y. Wang and K. Jacobi (in preparation).
- ²¹B. G. Frederick, T. S. Jones, P. D. A. Pudney, and N. V. Richardson, *J. Electron Spectrosc. Relat. Phenom.* **64/65**, 825 (1993).
- ²²D. C. Seets, M. C. Wheeler, and C. B. Mullins, *J. Chem. Phys.* **103**, 10 399 (1995).
- ²³S. T. King, *J. Phys. Chem.* **75**, 405 (1971).
- ²⁴J. E. Parmeter, U. Schwalke, and W. H. Weinberg, *J. Am. Chem. Soc.* **110**, 53 (1988).
- ²⁵H. Hinrichsen, *Catal. Today* **53**, 177 (1999).
- ²⁶H. Dietrich, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **105**, 8944 (1996).