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The adsorption of NH₃ on Rh(111)

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Abstract

The adsorption of NH₃ on Rh(111) has been investigated by temperature programmed desorption, work function measurements, low energy electron diffraction and secondary ion mass spectrometry. TPD indicates the existence of three distinct desorption states; α₁-, α₂- and β-NH₃ with peak maxima at 320, 155 and 130 K, respectively. For the most strongly chemisorbed state, α₁-NH₃, the desorption energy is 81.5 kJ mol⁻¹. A (2 × 2) LEED pattern is observed after complete filling of the α₁- and α₂-NH₃ states, which is attributed to saturation of the first adsorption layer, corresponding to an NH₃ coverage of 0.25 ML. The sticking coefficient for NH₃ adsorption at 120 K, is on the order of unity and independent of coverage during filling of the first adsorption layer. NH₃ adsorption causes a significant work function decrease of 2.4 eV below the value of clean Rh(111). The initial work function decrease corresponds to an average dipole per NH₃ molecule of 1.9 D, i.e. higher than that of the NH₃ molecule in the gas phase. SIMS spectra of NH₃ on Rh(111) contain Rh(NH₃)⁺ as the predominant ammonia-derived cluster ion. The intensity of the Rh(NH₃)⁺ cluster ion behaves strongly non-linear with the NH₃ coverage and indicates some changes in the NH₃ adlayer at a coverage of ≈0.12 ML.

Keywords: Ammonia; Chemisorption; Low energy electron diffraction (LEED); Rhodium; Secondary ion mass spectroscopy; Single crystal surfaces; Thermal desorption spectroscopy; Work function measurements

1. Introduction

Understanding the adsorption and the reactivity of NH₃ on rhodium surfaces is of interest for large scale industrial processes. Both the HCN synthesis, according to the Andrussow process [1], and the formation of NO by oxidation of NH₃, known as the Ostwald process [2] are realized on Pt–Rh catalysts. Furthermore, formation of NH₃ has been considered as a possibility in the reduction of NO by H₂ in the context of automotive exhaust catalysis [3].

Surprisingly little has been reported in the literature about the interaction between NH₃ and rhodium. In contrast to the other transition metals, the attention has been focused mainly on the decomposition of NH₃ in the moderate pressure regime [4–6]. Table 1 summarizes what is known about adsorption of NH₃ on rhodium. The results reported so far suggest that NH₃ decomposes at least partially on defect-rich rhodium surfaces, such as wires and foils, but stays intact on the close-packed (111) surface. Evidence for NH₃ dissociation on the faceted surface of a rhodium field emitter tip was only found when adsorption took place at elevated temperature, as reported by Van Tol et al. [7]. Noteworthy is the formation of N₂H₂, found by Prasad and Gland [8], and attribu-
Table 1

<table>
<thead>
<tr>
<th>Rhodium substrate</th>
<th>NH₃ adsorption temperature (K)</th>
<th>Surface species</th>
<th>Evidence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire</td>
<td>300–450</td>
<td>N, NHₓ, H</td>
<td>NH₃reaction-limited H₂ desorption at 420 K</td>
<td>[9]</td>
</tr>
<tr>
<td>Foil</td>
<td>80</td>
<td>NHₓ, NH₃, H</td>
<td>N₂, N₂Hₓ, and NH₃ desorption</td>
<td>[8]</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>100</td>
<td>NH₃</td>
<td>NH₃ desorption only</td>
<td>[10,11]</td>
</tr>
<tr>
<td>Rh tip</td>
<td>80–300</td>
<td>NH₃</td>
<td>Image clean tip appears at 400 K</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>&gt;400</td>
<td>N, NHₓ, H</td>
<td>Tip clean above 650 K due to N₂ desorption</td>
<td>[7]</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>120</td>
<td>NH₃</td>
<td>NH₃ desorption only, SIMS</td>
<td>This work</td>
</tr>
</tbody>
</table>

uted to the recombination of imide (NH_ads) surface intermediates.

More complete pictures of NH₃ adsorption exist for the transition metals Ni, Pt, Ru, Cu and Ag, for which results have briefly been summarized by Thornburg and Madix [12]. The adsorption behaviour of NH₃ on the various metals shows large similarities. The NH₃–Ru(0001) system has been studied in greatest detail and will therefore be briefly reviewed here.

TPD experiments indicate four distinct desorption states of NH₃ from Ru(0001) [13,14]. The first two states, denoted α₁- and α₂-NH₃, have peak maxima at 315 and 180 K, respectively. Complete filling of these two states leads to saturation of the first adsorption layer and yields a sharp (2 × 2) LEED pattern corresponding to a coverage of 0.25 ML. ESDIAD results show that in the α₁-state, which saturates at ≈0.15 ML, NH₃ is adsorbed with its Cᵥ symmetry axis perpendicular to the surface; the molecules are either rotating freely around the perpendicular axis or possess a random azimuthal orientation [14]. Filling of the α₂-state leads to some tilting of the molecules with respect to the surface normal. Further increase of the NH₃ coverage results in the formation of a second adsorption layer, which gives rise to a sharp desorption peak at 130 K, denoted β-NH₃. During filling of the second adsorption layer a (2√3 × 2√3)R30° LEED pattern is observed. For this ordered structure a model is proposed in which all first layer molecules, 0.25 ML, occupy three fold sites on which 0.08 ML of "second layer" or β-NH₃ is adsorbed through hydrogen bonding [14]. The formation of multilayers, γ-NH₃, commences at coverages in excess of 0.50 ML, and is readily observed by a desorption peak at 115 K.

The work function of the NH₃/Ru(0001) surface decreases linearly with coverage during the filling of the α₁-state. It diminishes further, with a decreasing slope, as the α₂- and β-states populate, to reach a maximum value of Δϕ = −2.4 eV after complete filling of the β-state.

EELS and RAIRS measurements confirm the existence of various adsorption states of NH₃ on Ru(0001) [13,15]. The IR-cross section for the NH₃ deformation mode appears to behave strongly non-linear with coverage. During filling of the α₁-NH₃ state the absorption increases linearly with coverage, but formation of α₂-NH₃ reduces the cross section and completion of the β-NH₃ state, thought to occur through H-bonding, quenches the deformation mode entirely. The purpose of this paper is to characterize the adsorption of NH₃ on Rh(111) by temperature programmed desorption (TPD), low energy electron diffraction (LEED), work function measurements and static secondary ion mass spectrometry (SIMS). Results of the latter technique are included to serve as a reference for a subsequent kinetic study on the hydrogenation of atomic nitrogen on Rh(111), in which the SIMS technique successfully identifies intermediates [16].

2. Experimental

TPD, SIMS and work function experiments were performed in a stainless steel ultra high vacuum (UHV) system, pumped with a 360 l s⁻¹ turbomolecular pump and a water-cooled titanium sublimation pump. The base pressure was typically around 5 × 10⁻¹¹ mbar, and mass spectra of the residual gas indicated the presence of mainly H₂, CO and
CO₂. The system is equipped with a Leybold SSM 200 quadrupole mass spectrometer for TPD and SIMS, and a Leybold EA 10 hemisphere energy analyzer, for AES and $\Delta \Phi$ measurements. Both analyzers were interfaced with a PC for data storage.

SIMS measurements were performed in the static (low damage) mode. Typically, we used a defocussed 5 keV primary Ar⁺ beam with a current density of 1–10 nA cm⁻². To average eventual anisotropies in the secondary ion emission process we applied a target bias of +45 V and an extractor voltage of −300 V on the entrance lens of the quadrupole system.

Work function changes were determined by measuring the shift of the low kinetic energy onset of the secondary electron emission in AES. In order to minimize damage effects due to electron irradiation, we used a primary electron beam of 500 eV and 0.02 μA. The sample was biased −10 V with respect to the ground potential. The onset was defined as the energy at which the derivative of the secondary electron distribution maximizes. The shifts are reported with respect to the clean Rh(111) surface (5.6 eV) [17].

LEED experiments were performed in a different UHV system equipped with a Leybold Quadruvac Q100 mass spectrometer and a reverse view, four grid AES/LEED optics (Spectaleed, Omicron Vakuumphysik GmbH). LEED data were obtained with an electron beam current between 20 and 30 μA.

Each UHV system contained a rhodium crystal which was cut in the [111] orientation within 0.5° and polished by standard procedures. The temperature was measured by a chromel–alumel thermocouple spotwelded on the back of the crystal. The standard cleaning procedure consisted of an argon sputter treatment (900 K, 1.5 keV, 5 μA cm⁻²) followed by annealing in 2.10⁻⁸ mbar O₂ (900–1100 K) and a final annealing treatment in vacuum at 1420 K. The gases, NH₃ (UCAR electronic grade, 99.995%) and D₂ (Messer Griesheim, 99.7%) were used without further treatment. Exposures are reported in langmuirs (1 L = 1.33 x 10⁻⁶ mbar.s) and coverages are expressed with respect to the number of Rh surface atoms (1 ML = 16 x 10¹⁴ cm⁻²).

3. Results

3.1. Temperature programmed desorption

After adsorption of NH₃ at 120 K, temperature programmed desorption spectra were measured at a heating rate of 5 K s⁻¹, by monitoring the mass channels m/e = 2 (H₂), m/e = 17 (NH₃), m/e = 28 (N₂) and m/e = 30 (N₂H₂). In all cases, NH₃ was the only detectable N-containing desorption product. Some H₂ desorption was observed which was attributed to adsorption of small amounts of H₂ from the background.

The NH₃ desorption spectra in Fig. 1 show three distinct desorption states depending on the NH₃
coverage. The first low coverage state, denoted by \( \alpha_1 \text{-NH}_3 \), has a maximum around 320 K which broadens significantly to lower temperature with increasing \( \text{NH}_3 \) coverage. Note that the spectra contain a small shoulder to higher temperatures, which grows with increasing exposure. The origin of this signal is not clear; possible explanations will be given in the discussion section.

Application of the Redhead method [18] to the low coverage peak at 320 K yields a desorption energy of \( 81.5 \pm 3 \text{ kJ mol}^{-1} \) for \( \alpha_1 \text{-NH}_3 \), if a pre-exponential factor of \( 10^{13} \text{ s}^{-1} \) is assumed. Other analysis methods which in general give more reliable answers [19], appeared unsuitable because of the strong dependence of the desorption energy on the coverage.

The transition to the second desorption state \( \alpha_2 \text{-NH}_3 \), which maximizes at 155 K, takes place very gradually. Above \( \text{NH}_3 \) exposures of \( \approx 0.45 \text{ L} \), a third desorption state, \( \beta \text{-NH}_3 \), is observed by a very sharp peak at 130 K. Application of the Redhead method yields a desorption energy of \( 32 \text{ kJ mol}^{-1} \) for this \( \beta \text{-NH}_3 \), if a pre-exponential factor of \( 10^{13} \text{ s}^{-1} \) is assumed.

3.2. \( \text{D}_2 \) coadsorption

The fact that none of the experiments showed any traces of desorbing \( \text{N}_2 \) or \( \text{N}_2\text{H}_2 \) suggests that \( \text{NH}_3 \) adsorbs exclusively intact. In order to confirm this, some TPD experiments were done after coadsorption of \( \text{D}_2 \) and \( \text{NH}_3 \). If ammonia decomposes on the surface, and recombines upon desorption, \( \text{NH}_3-x\text{D}_x \) would be expected in the gas phase. Deuterated products did not form, however. \( \text{D}_2 \), \( \text{NH}_3 \) and small amounts of HD were the only desorption products observed, see Fig. 2.

The presence of HD indicates that some hydrogen was present on the surface also. Since the shape of the HD desorption peak is approximately the same as that of \( \text{D}_2 \) (see Fig. 2) it is most likely that this hydrogen stems from background adsorption. The small difference in the peak maximum of HD and \( \text{D}_2 \) (\( \approx 10 \text{ K} \)) is in line with the isotope shift that is observed when comparing \( \text{H}_2 \) and \( \text{D}_2 \) desorption. Coadsorption of \( \text{D}_2 \) appears to destabilize adsorbed ammonia: The \( \text{NH}_3 \) peak maximum shifted from \( \approx 300 \) to 265 K when 1.0 L \( \text{D}_2 \) was post dosed to a surface covered by 0.06 ML of \( \text{NH}_3 \), as Fig. 2 shows.

3.3. LEED of \( \text{NH}_3/\text{Rh(111)} \)

LEED experiments have been done to provide a calibration point for the \( \text{NH}_3 \) coverages. Fig. 3 shows the (1x1) LEED pattern of the clean \( \text{Rh(111)} \) surface and the (2x2)-\( \text{NH}_3 \) LEED pattern observed after dosing 0.45 L \( \text{NH}_3 \). The visibility of the (2x2) pattern depends strictly on the \( \text{NH}_3 \) coverage and arises only at a coverage obtained after a 0.45 L exposure, or after higher exposures followed by heating to 150 K. We therefore conclude that the (2x2) \( \text{NH}_3/\text{Rh(111)} \) structure is uniquely associated with completely filled \( \alpha_2 \)- and \( \alpha_1 \)-states. The applied beam energy was 58 eV in both cases and the temperature was 120
We assign the \((2 \times 2)\) pattern to an \(\text{NH}_3\) surface coverage of 0.25 ML, corresponding to a fully occupied \(\alpha_1\)- and \(\alpha_2\)-state. Similar assignments were made for \(\text{Ru}(0001)\) [14], \(\text{Ni}(111)\) [21] and \(\text{Pt}(111)\) [22].

3.4. Coverage calibration and sticking coefficient

Fig. 4 shows the \(\text{NH}_3\) uptake curve which was constructed by integrating the \(\text{NH}_3\) TPD peak areas and using the calibration point that the TPD area obtained after 0.45 L exposure corresponds to 0.25 ML. During the filling of the \(\alpha_1\)- and \(\alpha_2\)-\(\text{NH}_3\) states, the \(\text{NH}_3\) coverage increases linearly with \(\text{NH}_3\) exposure which implies that the sticking coefficient is independent of the coverage. We estimate that the initial sticking coefficient is close to unity. However, uncertainty in the total pressure measurement precludes an accurate assessment.

During the filling of the second adsorption layer above 0.25 ML, the scatter in the data enlarges and the uptake curve starts to deviate from linearity. This is probably due to larger errors that derive from integrating the sharp desorption peak at 130 K. Also evaporation of \(\text{NH}_3\) may become important since the adsorption temperature of 120 K is just below the desorption temperature of \(\text{NH}_3\) in the second layer, 130 K. Multilayers were not observed since this requires adsorption temperatures below 110 K.

3.5. Work function measurements

Fig. 5 shows the change of the work function versus the \(\text{NH}_3\) coverage. Up to an \(\text{NH}_3\) coverage of \(\approx 0.15\) ML, where the \(\alpha_1\)-state prevails, the work function decreases linearly with \(\text{NH}_3\) coverage. The initial slope, indicated by the solid line in Fig. 5, equals \(-11.5\) eV ML\(^{-1}\). For \(\text{NH}_3\) coverages between 0.15 and 0.25 ML, where the \(\alpha_2\)-state becomes occupied, the work function decrease becomes less pronounced. For \(\text{NH}_3\) coverages in excess of 0.25 ML, corresponding to the \(\beta\)-state, the work function becomes constant and reaches a saturation value of \(-2.4\) eV below the value of clean \(\text{Rh}(111)\).

K. We stress that under our conditions the \((2 \times 2)\) pattern was observable only for a few seconds. \(\text{NH}_3\) decomposition by electrons is well known [20], but also local heating may contribute to the rapid disappearance of the \((2 \times 2)\) LEED pattern.
3.6. Secondary ion mass spectrometry

Fig. 6 shows three characteristic mass regions of a SIMS spectrum of the Rh(111) surface covered with 0.10 ML of NH$_3$ at 120 K. The presence of NH$_3$ on the surface is best illustrated by the appearance of the Rh(NH$_3$)$^+$ cluster ion at $m/e = 120$. In the low mass region the predominant features are H$^+$ and NH$_2^+$ stemming from NH$_3$ fragmentation during the emission process. Comparable NH$_3$ fragmentation was observed in a previous SIMS study on the adsorption of NH$_3$. 

Fig. 5. The work function change as a function of the NH$_3$ coverage. The solid line indicates the initial work function decrease which equals $-11.5$ eV ML$^{-1}$. The slope of the curve decreases around an NH$_3$ coverage of $\sim 0.15$ ML, the maximum decrease is $-2.4$ eV.
on Fe(110) by Drechsler et al. [23]. The appearance of NH$_4^+$ is attributed to recombination of NH$_3$ and H in the near surface region during emission. The right panel of Fig. 6 shows the mass region associated with the emission of Rh$_2$-related clusters. Although the intensities are close to the noise level, both the Rh$_2^+$ and Rh$_2$(NH$_3$)$_x^+$ clusters ions can be recognized at $m/e = 206$ and 223, respectively. The nature of the signals in the region from $m/e = 212$ to 214 is unclear, but might be due to the Pt(NH$_4$)$_x^+$ cluster ions of the three Pt isotopes since Pt is a known trace impurity of rhodium.

We note in particular that SIMS gives no evidence for the presence of any dehydrogenated NH$_x$ species on the surface. Studies on the hydrogenation of adsorbed N-atoms revealed that such species can be detected in SIMS [16]. The SIMS data thus confirm the intact adsorption of NH$_3$ on the Rh(111) surface.

The study of the NH$_3$-Rh(111) adsorption system by SIMS is somewhat complicated by the fact that the work function of the surface decreases significantly upon increasing NH$_3$ coverage. A work function decrease generally results in a higher neutralization probability of the emitted secondary ions [24,25] which results in a decrease of the SIMS peak intensities. In practice only the Rh(NH$_3$)$_x^+$ cluster ion has enough intensity to give reliable information about the NH$_3$-Rh(111) system in a broad coverage regime.

The left panel of Fig. 7 shows some characteristic SIMS spectra in the mass region from $m/e = 100$ to 125 of the Rh(111) surface for various NH$_3$...
Fig. 7. The left panel shows SIMS spectra of the Rh(111) surface for some characteristic NH₃ coverages at 120 K. The right panel shows the decrease of the absolute Rh⁺ peak with increasing NH₃ coverage. The work function decrease is shown for comparison. The SIMS Rh(NH₃)⁺/Rh⁺ peak intensity ratio is a strongly non-linear function of the NH₃ coverage.

Temperature programmed SIMS experiments were carried out to monitor the various NH₃ adsorption states as a function of the temperature and initial coverage. Fig. 8 shows the Rh(NH₃)⁺/Rh⁺ intensity ratio as a function of the temperature. The upper spectrum is obtained starting from an NH₃ coverage of 0.50 ML, where...
Fig. 8. Temperature programmed SIMS spectra showing the Rh(NH$_3$)$_n$/$Rh^+$ peak intensity ratio as a function of the temperature for various initial NH$_3$ coverages. The heating rate was 5 K s$^{-1}$. The desorption of the second adsorption layer at 130 K is clearly illustrated by the upper spectrum. Desorption of $\alpha_2$-NH$_3$ can not be observed, $\alpha_1$-NH$_3$ desorption above 300 K is observed by all spectra.

both $\alpha_1$, $\alpha_2$- and $\beta$-NH$_3$ are present. The desorption of NH$_3$ from the $\beta$-state is clearly demonstrated by the decrease of the Rh(NH$_3$)$_n$/$Rh^+$ peak intensity ratio at about 130 K. Both the upper and middle spectrum show that NH$_3$ desorption in the temperature regime between 150 and 260 K does not result in a significant change of the Rh(NH$_3$)$_n$/$Rh^+$ intensity ratio. However, above 260 K the intensity ratio starts to increase again and reaches a maximum at 310 K. The decrease of the Rh(NH$_3$)$_n$/$Rh^+$ ratio above 310 K is illustrated by all spectra and corresponds to the desorption of $\alpha_1$-NH$_3$ which is present on the surface up to temperatures of 370 K.

4. Discussion

4.1. Adsorption states of NH$_3$

The adsorption of NH$_3$ on Rh(111) greatly resembles that on the hexagonally close-packed surfaces of other group VIII metals, such as Pt(111), Ru(0001) and Ni(111). This is most prominently shown by the respective temperature programmed desorption data. Table 2 presents an overview of the different desorption states and the corresponding peak maximum temperatures for NH$_3$ on these metals. Note, however, that different authors used different heating rates, implying that the peak temperatures in Table 2 can only serve as a rough guide for comparison.

The high temperature desorption state $\alpha_1$-NH$_3$ is observed for all the metals and also the broadening of the $\alpha_1$-NH$_3$ desorption peak towards lower temperature with increasing NH$_3$ coverage is a common feature. The $\alpha_2$-NH$_3$ desorption state, which occurs on Ru(0001) at about 180 K and on Rh(111) at about 155 K, does not stand out as a separate peak in the desorption of NH$_3$ from Ni(111) and Pt(111). The separation between the $\alpha_1$- and $\alpha_2$-NH$_3$ states is a bit arbitrary anyway, as the transition between the two is rather gradual. Benndorf et al. [14] take 0.15 ML of NH$_3$ on Ru(0001) as the coverage where the $\alpha_1$-state saturates and the $\alpha_2$-state starts to form. This is in good agreement with what we find for the TPD of NH$_3$ from Rh(111) in Fig. 1. In addition, 0.15 ML is also a coverage where the work function changes its slope and the Rh(NH$_3$)$_n$/$Rh^+$ intensity ratio shows a sharp decrease. Both observations support the notion of a discontinuity in structure at 0.15 ML of NH$_3$.

The $\beta$-NH$_3$ desorption state, associated with desorption from a "second" adsorption layer, is observed on all metals by the appearance of a sharp desorption peak in the temperature range between 130 and 160 K. We did not observe the formation of the $\gamma$-NH$_3$ state corresponding to multilayers, since the adsorption temperature of 120 K employed here is just above the $\gamma$-NH$_3$ desorption temperature of 100–115 K.

The TPD experiments gave no indication of NH$_3$ decomposition. This was evidenced by the
Table 2
Comparison of the desorption maxima, maximum work function change $\Delta \Phi_{\text{max}}$ and average initial dipole $\mu$ of NH$_3$ for some group VIII metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>TPD peak maximum temperature* (K)</th>
<th>$\Delta \Phi_{\text{max}}$ (eV)</th>
<th>$\mu^{**}$ (D)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_1$-NH$_3$</td>
<td>$\alpha_2$-NH$_3$</td>
<td>$\beta$-NH$_3$</td>
<td>$\gamma$-NH$_3$</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>320</td>
<td>155</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>Ru(001)</td>
<td>310</td>
<td>180</td>
<td>130</td>
<td>115</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>360</td>
<td>-</td>
<td>160</td>
<td>110</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>290</td>
<td>-</td>
<td>145</td>
<td>-</td>
</tr>
</tbody>
</table>

*Note that the heating rates were not the same in the different studies.

**The dipole moment of the free NH$_3$ molecule is 1.47 D.

complete absence of any decomposition products, and by the D$_2$ coadsorption experiments. If any NH$_3$ decomposition did take place during heating this would have been reflected in the HD desorption spectra. However, the HD trace closely follows the D$_2$ desorption (Fig. 2) indicating that the ratio between hydrogen and deuterium on the surface remains constant. This confirms that there is no production of surface hydrogen by decomposition of NH$_3$. Also the NH$_3$ TPD studies on Ru(0001), Pt(111) and Ni(111) show that desorption is highly favoured above dissociation, provided adsorption of NH$_3$ is done at low temperatures. Even on Ru(0001), expected to be the most reactive metal, not more than 3% of the adsorbed NH$_3$ was found to dissociate [15].

In addition to the three distinct desorption states, the NH$_3$ TPD spectra of Fig. 1 show a small high temperature tail which extends from 340 to 380 K. The TPSIMS spectra reveal that in this temperature range there is still some NH$_3$ on the surface. The most obvious explanation for the desorption tail would be limited pumping speed, caused by adsorption of NH$_3$ on the UHV chamber walls, resulting in some readsorption on the rhodium surface. In principle the NH$_3$ desorption tail might be due to decomposition and rehydrogenation, but this explanation is invalidated by the absence of H–D exchange in NH$_3$ in the coadsorption experiments with D$_2$. As the amount of NH$_3$ desorbing in this tail accounts for less than 1% of a monolayer, we can also not exclude that defects play a role.

4.2. Effective dipole moment of adsorbed NH$_3$

Adsorption of ammonia results in a significant lowering of the work function. Gas phase NH$_3$ has a dipole moment of 1.47 D [30]. As NH$_3$ is bonded to the substrate via the lone pair of the nitrogen atom, a work function decrease is expected on the basis of the orientation of the dipole on the surface.

The Helmholtz equation [31] translates the initial work function change to an average dipole moment of the adsorbate:

$$\bar{\mu} = \frac{\varepsilon_0 |\Delta \Phi|}{\sigma},$$

where $\bar{\mu}$ = average dipole moment [D]; $|\Delta \Phi|$ = work function change [eV]; $\varepsilon_0$ = electric permittivity of vacuum [D·cm$^{-2}$·eV$^{-1}$]; $\sigma$ = adsorbate concentration [cm$^{-2}$]. Inserting the initial work function decrease of $-11.5$ eV ML$^{-1}$, and using $\varepsilon_0 = 2.66 \times 10^{14}$ D·cm$^{-2}$·eV$^{-1}$, and $\sigma = 16 \times 10^{14}$ cm$^{-2}$·ML$^{-1}$, we find an average dipole of 1.9 D for the NH$_3$ molecule at low coverage. This value is about equal to the dipole moments calculated in the same way for NH$_3$ on Ru(0001) [14] and Pt(111) [22], as Table 2 shows. It should be noted that the Helmholtz equation attributes the work function change entirely to charge separation in the adsorbate molecule, which is not necessarily true since also charge transfer between the adsorbate and the substrate has to be considered. However, the fact that the calculated effective dipole of adsorbed NH$_3$ (1.9 D) is stronger than in the free molecule (1.47 D), indicates that
charge transfer from NH₃ to the substrate, or an enhancement of the NH₃ dipole upon adsorption, or a combination of these factors plays a role.

4.3. Coverage dependent effects

The outstanding coverage dependent effect in the adsorption of NH₃ on Rh(111) is the dramatic decrease of the α₂-NH₃ desorption temperature with increasing NH₃ coverage. Formerly, this broadening has entirely been attributed to a decrease of the desorption energy caused by repulsive lateral interactions between NH₃ molecules [14]. If a constant prefactor was assumed the desorption behaviour could be described by assuming the desorption energy $E_{\text{des}}$ to obey the following functional form:

$$E_{\text{des}} = E_{\text{des}, 0} - W \cdot \theta^{3/2}. \quad (2)$$

A problem with the above described explanation is that the dramatic influence of the coverage on the desorption energy is by no means recognized in the coverage dependent behaviour of the work function. Up to a coverage of $\approx 0.15$ ML, the work function decreases linearly with the NH₃ coverage, implying that the work function change and, consequently, the average dipole per adsorbed NH₃ molecule is constant. If repulsive lateral interactions are responsible for the large decrease in the desorption energy also the average dipole of the NH₃ molecules is expected to be influenced. We therefore wonder if entropy effects could be responsible. In the framework of Eyring's transition state theory, the rate of desorption is written as [32]:

$$r_{\text{des}} = \frac{k_B T}{h} \frac{p_{\theta}^f}{p_{\text{f}}} e^{E_{\text{des}}/RT} \theta_{\text{NH₃}}, \quad (3)$$

where $r_{\text{des}} = \text{NH₃ desorption rate \ [ML s^{-1}]}$; $k_B = \text{Boltzmann's constant \ [J K^{-1}]}$; $T = \text{Temperature \ [K]}$; $h = \text{Planck's constant \ [J s]}$; $p_{\theta}^f = \text{partition function transition state \ [-]}$; $p_{\text{f}} = \text{partition function ground state \ [-]}$; $E_{\text{des}} = \text{desorption energy \ [J mol^{-1}]}$; $R = \text{gas constant \ [J mol^{-1} K]}$; $\theta_{\text{NH₃}} = \text{NH₃ coverage \ [ML]}$. If the adsorption energy and hence, $E_{\text{des}}$ is constant, as the constant work function decrease seems to suggest, then a coverage dependence of the desorption rate constant can still be caused by the ratio of the partition functions. For example, suppose that adsorbed ammonia molecules are mobile in the high temperature/low coverage regime of the TPD spectra, and that the transition state for desorption is mobile as well, then the ratio of the partition functions $p_{\theta}^f/p_{\text{f}}$ is on the order of 1 and the molecule desorbs with a pre-exponential factor on the order of $e \cdot k_B \cdot T/h = 10^{13} \text{ s}^{-1}$. As the coverage becomes higher, the translational partition function of the ground state decreases, while that of the transition state may remain high. In this respect, it is important to note that the sticking coefficient for adsorption in this coverage regime is constant and on the order of unity, which might point to the existence of a mobile precursor state of ammonia. The result is that the ratio $p_{\theta}^f/p_{\text{f}}$ in Eq. (3) increases, causing the pre-exponential to go up with coverage, while the adsorption energy may remain constant until the adsorbate molecules start to interact, in the α₂-state. Note that, if the above interpretation is correct, the estimate of the low coverage adsorption energy on the basis of the Redhead formula, 81 kJ mol⁻¹, should be correct, as the pre-exponential factor would indeed be on the order of $10^{13} \text{ s}^{-1}$.

The decrease of the work function change versus coverage at 0.15 ML corresponds to the occupation of the α₂-NH₃ state, where lateral interactions between adsorbed NH₃ molecules become important. This correlates well with the ESDIAD results on Ru(0001), which indicate that NH₃ tilts above a coverage of 0.15 ML [14]. Although tilting of the NH₃ molecules results in a decrease of the effective dipole moment, mutual depolarization caused by lateral interactions between the NH₃ molecules is expected as well. After adsorption of 0.25 ML of NH₃, the average dipole per NH₃ molecule is 1.60 D, which is significantly lower than the initial value.

4.4. SIMS of NH₃ on Rh(111)

The most striking result from the SIMS experiments is the strongly non-linear behaviour of the Rh(NH₃)⁺/Rh⁺ ratio as a function of the ammonia coverage. A complete explanation of the SIMS intensities is difficult to give, since the emission
process of secondary ions is highly complex and not fully understood. Nevertheless, it is instructive to discuss the intensities in the light of the changing work function (right panel Fig. 7) on the basis of Norskov and Lindquist's perturbation model [33]. The latter states that the ionization probability which predominantly determines the positive secondary ion yield can be written as:

\[ R^+ \propto e^{\frac{\phi - \phi_s}{v_\perp}} \]

where \( R^+ \) = the ionization probability of \( R^- \); \( \phi \) = work function of the substrate [eV]; \( \phi_s \) = ionization energy of \( R^- \) [eV]; \( v_\perp \) = normal velocity of the sputtered particle [m s\(^{-1}\)]. The rational behind the equation is that the work function affects the neutralization probability of the secondary ion during the emission process.

The decreasing yield of the Rh\(^+\) ion as shown in the right panel of Fig. 7 is straightforwardly explained by the decreasing work function when the surface fills with ammonia. It should be realized, however, that the observed correlation can only be qualitative since the property of interest is not the macroscopic work function of the surface, but the local surface potential or the local work function. Calculations by Janssens et al. [34,35] on the electrostatic surface potential of an ordered array of dipoles, chosen to represent the adsorption of potassium on Rh\((111)\), provide at least a qualitative guide for the situation of NH\(_3\) on Rh\((111)\). In the limit of low NH\(_3\) coverage, each molecule decreases the work function on the adsorption site and on the nearest neighbour rhodium atoms. The strong local variations in the work function complicate the interpretation of the emission behaviour of the Rh(NH\(_3\))\(^+\) cluster ions. However, in the low coverage regime, where mutual interactions between the NH\(_3\) molecules are of minor importance, the intensity of the Rh(NH\(_3\))\(^+\) signal is expected to be proportional to the NH\(_3\) coverage, which is indeed the case. The question remains why the Rh(NH\(_3\))\(^+\)/Rh\(^+\) ratio shows a sharp decrease around an NH\(_3\) coverage of \(\approx 0.12\) ML. It seems obvious that this is caused by increasing interactions between the NH\(_3\) molecules. Whether the decrease of the Rh(NH\(_3\))\(^+\)/Rh\(^+\) ratio is due to local work function effects, to changes in the adsorption geometry or to bonding between the NH\(_3\) molecules, cannot be answered from these experiments. However, in this respect it should be mentioned that the non-linear behaviour of the SIMS Rh(NH\(_3\))\(^+\)/Rh\(^+\) intensity ratio versus the NH\(_3\) coverage shows some resemblance with the non-linear behaviour of the IR cross section of the NH\(_3\) umbrella mode with NH\(_3\) coverage as reported for Ru\((0001)\) [13]. The drop in the IR cross section, which was observed at an NH\(_3\) coverage of \(\approx 0.15\) ML, was attributed to tilting of the NH\(_3\) molecules and the formation of hydrogen bonds for higher coverages.

SIMS is extremely sensitive towards NH\(_3\) in the low coverage regime, NH\(_3\) coverages below 0.01 ML can easily be detected. This makes SIMS very suitable to detect small traces of NH\(_3\) on the surface under reaction conditions.

4.5. Adsorption site of NH\(_3\)

The adsorption site of the \(\alpha_1\)-NH\(_3\) on the transition metals is still under debate. Ab initio calculations on Ni\((111)\) show that the adsorption energies of NH\(_3\) in the on-top site, the fcc three fold site and the twofold or bridge site are very similar, 79, 75 and 71 kJ mol\(^{-1}\), respectively [36]. Tentatively, the fcc site has been suggested for Ni\((111)\) [21] and Pt\((111)\) [22] while on Ru\((0001)\) both the on-top [15] and the fcc site [14] have been proposed. Brown and Vickerman [26] have demonstrated that SIMS intensity ratios yield information on the adsorption site of simple adsorbate molecules such as CO and NO. Unfortunately, it is not possible to determine the distribution of NH\(_3\) over Rh\(^+\), Rh\(_2^+\) and Rh\(_3^+\) clusters because of intensity limitations. Nevertheless, we tend to favour adsorption of NH\(_3\) in the on-top site, since the Rh(NH\(_3\))\(^+\) cluster ion is observed very explicitly.

5. Conclusions

Adsorption of NH\(_3\) on Rh\((111)\) greatly resembles that on the hexagonally close packed surfaces of Pt, Ru and Ni. NH\(_3\) adsorbs molecularly on
Rh(111) at 120 K and no evidence for any decomposition or H–D exchange is found during heating.

The NH₃ desorption behaviour shows a very explicit coverage dependence. At low coverage α₁-NH₃ desorption is observed at 320 K, corresponding to a desorption energy of 81.5 kJ mol⁻¹. Gradual broadening of the α₁-NH₃ desorption state to lower temperature results in a smooth transition to the second desorption state α₂-NH₃ at 155 K. Filling of the α₁- and α₂-NH₃ states yields a sharp (2×2) LEED pattern which we attribute to completion of the first adsorption layer and an NH₃ coverage of 0.25 ML. The sticking coefficient of NH₃ at 120 K is close to unity and independent of the coverage during filling of the first adsorption layer. Desorption of 13-NH₃ occurs at 130 K.

During filling of the α₁-state the work function decreases linearly with coverage, the dependence levels off during filling of the α₂-state and a maximum decrease of −2.4 eV is found after completion of the first adsorption layer. The enlargement of the average dipole of NH₃ from 1.47 to 1.9 D upon adsorption indicates that either charge transfer from NH₃ to the substrate or enlargement of the NH₃ dipole or both has to take place.

The presence of NH₃ on the surface is clearly evidenced by the appearance of the Rh(NH₃)⁺/Rh⁺ peak intensity ratio shows non-linear behaviour with the NH₃ coverage and indicates some structural changes in the adlayer at a coverage of ≈0.12 ML.

SIMS appears to be very sensitive for NH₃, coverages below 0.01 ML can easily be detected. TPSIMS experiments confirm that desorption of the second adsorption layer occurs at 130 K. Also the desorption of α₁-NH₃ is observed and it becomes clear that some NH₃ is present on the surface up to 370 K during TPD.

References