

ADSORPTION AND THERMAL DECOMPOSITION OF AMMONIA ON A Ni(110) SURFACE: ISOLATION AND IDENTIFICATION OF ADSORBED NH_2 AND NH

I.C. BASSIGNANA *, K. WAGEMANN, J. KÜPPERS and G. ERTL

Institut für Physikalische Chemie, Universität München, D-8 München 2, Fed. Rep. of Germany

Received 20 February 1986; accepted for publication 9 April 1986

The adsorption and thermal decomposition of ammonia at a Ni(110) surface was studied by means of thermal desorption (TD) and high resolution electron energy loss (HREEL) spectroscopy in the temperature range 110–500 K. Low temperature adsorption ($T < 186$ K) revealed only molecular adsorbed ammonia, including multilayer formation at 110 K. HREEL spectra taken after exposing the surface to NH_3 in the range 300 to 400 K for the first time confirmed the presence of NH_2 and NH fragments at the surface. It proved necessary to collect the HREEL spectra at elevated temperatures in order to prevent molecular readsorption and allow an unequivocal determination of the fragments vibration frequencies. From TD spectra it is concluded that both fragments are unstable and decompose. NH_2 fragmentation into $\text{NH} + \text{H}$ and $\text{N} + 2\text{H}$ as monitored by H_2 desorption occurs around 430 K, NH fragmentation around 500 K. Beyond 550 K only atomic nitrogen is left at the surface. The activation energy for NH_2 decomposition was determined to be 20 kcal/mol from kinetic measurements. Fragmentation of NH_3 at low temperature may be induced by electron bombardment. Small quantities of coadsorbed oxygen ($\theta \approx 0.1$) destabilize both the NH_3 and the fragment species. This results in an accelerated decomposition reaction, but the fragments can still be identified by their vibration spectra.

1. Introduction

The identification of surface intermediates is of crucial importance for elucidating the mechanisms of heterogeneously catalyzed reactions. Although nickel is no suitable material for an ammonia synthesis catalyst (presumably because the sticking coefficient for dissociative nitrogen adsorption is too low), several reports on the characterization of surface species formed in the reverse reaction, viz. NH_3 decomposition, on a Ni(110) surface have recently been published [1–4,43].

Recent studies [1,2] indicate that it is possible to isolate or at least enrich the concentration of one fragment species over the other by controlling the

* Present address: Bell-Northern Research Ltd., Ottawa, Ontario, Canada.

dosing temperature and pressure. Other studies show that it is also possible to induce the decomposition of ammonia by either predosing the surface with oxygen [3] or by submitting the NH₃ covered surface to electron bombardment [4].

It was the aim of this investigation to prepare and identify by vibrational spectroscopy the fragment species which had been postulated previously on the basis of more indirect information. This seemingly simple mandate does not lend itself to a straightforward execution. Since NH₃ fragments are unstable and transient species, special precautions must be taken.

Several problems are inherent in any investigation of NH₃, not the least of which is the role played by the spectroscopy used and the conditions under which the system is investigated. A recent study [4] shows clearly that adsorbed NH₃ can be decomposed by bombardment of sufficiently energetic electrons. This fact should be born in mind when interpreting XPS, UPS, LEED and Auger spectra. HREELS with its very low energy for incident electrons is only a minor perturbation of the adsorbed phase and so is an ideal tool for investigating this particular system.

Experimental conditions also play a significant role. EELS spectra are conventionally taken at a temperature where the given species is known to adsorb. The effects of heating the surface are then usually observed by flashing the sample or annealing it for some time at the higher temperature but then the spectra are again taken at the lower temperature. This technique is adequate for most adspecies, however, in the case of ammonia where the pumping efficiency is poor, the sticking coefficient at low T is high, and the cross section for the most prominent vibration mode is also sizeable, readsorption can play a significant role. And indeed, since the concentration of the fragments is usually small and since their vibrational frequencies are not so very different from those of the parent NH₃ a minimal amount of readsorption can mask and so make the identification of fragment spectra difficult. The problem of readsorption is usually dealt with by using a doser, however, for ammonia this itself can be problematic.

In this work the problem was overcome by measuring EELS spectra at the higher temperatures in situ; we report here an experimental procedure for doing this.

A further attempt to identify decomposition fragments was also made by purposely decomposing the ammonia according to the prescribed methods of electron bombardment and oxygen precoverage.

2. Experimental

The experiments were performed in a UHV chamber equipped with LEED, AES, a quadrupole mass spectrometer and a rotatable single pass high

resolution electron energy loss spectrometer, as has been described elsewhere [5]. All spectra were recorded in the specular direction using a primary beam energy of 2.6 eV.

The Ni(110) sample was cleaned using Ar^+ ion bombardment followed by annealing to 950 K. The surface cleanliness was tested both by Auger spectroscopy and by examining the hydrogen TD spectra of a 1 L adlayer of H_2 . The peak shape of the hydrogen TD spectra in this coverage range is an extremely sensitive test of surface cleanliness. When the 1 L exposed surface gives the same TD peak shape as the saturation covered surface, fig. 4 inset, then the surface cleanliness is verified; this has been discussed previously [6].

The gases were introduced using variable leak valves and all dosing of the crystal was done via the background. All exposures are reported in nominal langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$). For ammonia these numbers are only meant as a guide. Since NH_3 was dosed via the background, the high sticking coefficient, the poor pumping efficiency, and the long measuring times for HREELS ($\sim 20 \text{ min}$) makes it highly probable that at least for the lowest coverages ($< 2 \text{ L}$) the effective exposure can be twice that reported here. The error at the higher coverages is, of course, proportionally smaller.

Ammonia has a very high sticking coefficient especially at the lower temperatures, consequently spectra taken at lower temperatures after having annealed at higher temperatures are never free of the lower temperature species: in this case molecular ammonia. Since the main thrust of this work was to isolate ammonia fragments which are present only at the higher temperatures, it was necessary to be able to record spectra in situ. Our computer-controlled data acquisition system made it possible to record HREEL spectra at temperatures up to about 800 K. This was accomplished using a heat-pause-measure cycle; this procedure was necessary as resistive heating of the sample causes too great a disturbance to the electron beam to permit simultaneous measurement. The time required for the heat and measure cycles depended on the temperature range in question. For a typical experiment in the temperature range 200–400 K the sample was resistively heated for approximately 14 s, paused for 2 s, and then spectra recorded for 7–14 s. This sequence was repeated until the required energy range had been scanned. For all of the experiments below 400 K the sample temperature never varied by more than 5 K from the reported value. Data accumulation has been performed in such a way that the whole spectral range in the loss spectra represent specific surface conditions.

3. Results and discussion

3.1. Adsorption of NH_3 at low temperature, $T < 190 \text{ K}$

A family of HREEL spectra measured after exposing increasing amounts of ammonia to the surface is shown in fig. 1. In the low frequency region, below

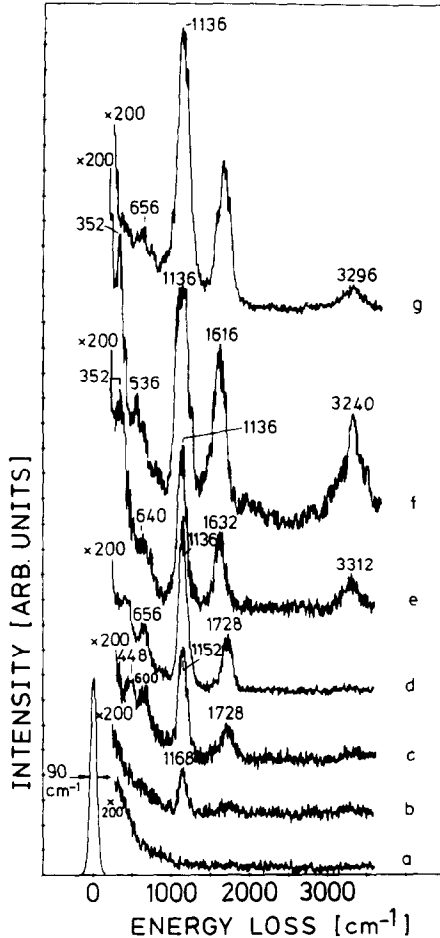


Fig. 1. HREEL spectra measured after dosing a clean Ni(110) surface (a) with increasing amounts of ammonia at 110 K, (b) 0.2 L, (c) 0.5 L, (d) 0.8 L, (e) 2.3 L, (f) 6.0 L, (g) after flashing the sample to 186 K.

1000 cm^{-1} , two losses are observed, shifting with coverage, placed at 450 and $600\text{--}650\text{ cm}^{-1}$ respectively. The most prominent loss peaks, also shifting with coverage, are placed at $\sim 1168\text{--}1136$ and $\sim 1730\text{--}1630\text{ cm}^{-1}$ respectively. High frequency vibrational structures are observed only when approaching the monolayer (spectrum e), documented by a broad structure at 3312 cm^{-1} . After the onset of multilayer formation (spectrum f) loss spectra exhibit an extremely sharp peak at 352 cm^{-1} , a broader one at 536 cm^{-1} , two almost equally intense peaks at 1136 and 1616 cm^{-1} , and finally a broad structure centered around 3240 cm^{-1} . After flashing off the multilayer structure by

Table 1
Group frequencies in ammonia complexes

Mode	Symmetry	Range (cm^{-1})
$\nu_d(\text{NH})$	E	3300–3400
$\nu_s(\text{NH})$	A_1	3200–3350
$\delta_d(\text{HNN})$	E	1500–1650
$\delta_s(\text{HNN})$	A_1	1100–1400
$\rho_r(\text{NH}_3)$	E	600– 950
$\nu(\text{Me-N})$	A_1	300– 550

raising the temperature to 186 K, the monolayer features are restored (spectrum g).

The assignment of the various loss peaks to vibrational modes of the adsorbate can be based on previous studies dealing with the $\text{NH}_3/\text{Ni}(110)$ or other systems. Much experimental evidence exists from which molecular adsorption at low temperatures has to be concluded [7]. Further it is known from ESDIAD [3] and ARUPS [2] studies that ammonia bonds via its lone pair orbital to the ridge atop nickel atoms, its threefold axis being normal to the surface, and the three hydrogen atoms pointing outwards. In this configuration the adsorbate complex can have C_{3v} or C_s symmetry, depending on the number of surface atoms involved. In either case a dipole active Ni–N stretch vibration is expected at low frequency. Accordingly we attribute the loss around 450 cm^{-1} to that mode. The next loss peak, placed at 600 cm^{-1} at low NH_3 coverage, is connected with the rocking mode, $\rho_r(\text{NH}_3)$, which is observed at similar frequencies for NH_3 on $\text{Pt}(111)$ [8] and $\text{Cu}(110)$ [9], namely at 720 and 570 cm^{-1} , respectively.

In a previous HREELS study of the $\text{NH}_3/\text{Ni}(110)$ system [7] the loss at 570 cm^{-1} was assigned to the Ni–N stretch mode, which we believe to be the ρ_r mode. Comparing with other NH_3/metal systems, and a variety of ammonia complexes, see table 1, the present interpretation seems more probable.

The two most prominent peaks, between 1000 and 2000 cm^{-1} , are identified by comparison with gaseous NH_3 as due to the symmetric and degenerate deformation modes, δ_s and δ_d , of the ammonia skeleton. As can be seen from table 1, the frequencies observed for these modes are in the range spanned by amino complexes. With other systems, e.g. $\text{Pt}(111)$ [8], $\text{Cu}(110)$ [9], $\text{Fe}(110)$ [10] the same assignment has been reported.

The high frequency loss, near 3300 cm^{-1} , has to be connected with the s and d $\nu(\text{N-H})$ vibrations, which are not resolved in the present case.

Three remarks should be added concerning the HREEL spectra measured up to monolayer coverage. Firstly, the δ_d mode is observed at low coverage at a comparatively high frequency, 1728 cm^{-1} ; only when the monolayer is completed its frequency is shifted to a more reasonable value, 1632 cm^{-1} . As

unwanted residual gas adsorption, in the present case H₂ and CO, has always to be dealt with, vibrations of these co-adsorbates may interfere with those of the primary adsorbate. Co-adsorption experiments indeed revealed that the C–O stretch vibration which is observed at 1960 cm⁻¹ at very low CO coverage (< 0.1 L exposure) shifts downward to 1760 cm⁻¹ when 0.1 L NH₃ is adsorbed afterwards. Due to this fact the low coverage value of the δ_a mode, 1728 cm⁻¹, seems to be incorrect. The high NH₃ coverage δ_a frequency, 1632 cm⁻¹, is less affected and therefore regarded as more reliable. The second remark refers to the low frequency loss region, below 1000 cm⁻¹. In that range M–C, M–O and M–H frequencies are observed and one has to ascertain that the frequencies given for the M–N and $\rho_r(\text{NH}_3)$ mode are not affected by such spurious effects. Carbon and oxygen can be ruled out as prior and subsequent to each ammonia adsorption measurement reference H₂ adsorption/desorption runs were made in order to check the surface cleanliness even beyond the capabilities of our AES equipment. Hydrogen, which would cause a M–H frequency at ~ 600 cm⁻¹ [11], has always been detected as a co-adsorbate in small quantities, but control experiments showed that these were too small to be responsible for the loss peak seen at that frequency with adsorbed ammonia. The last point refers to the intensity of the N–H stretch mode, which is very small in the present study. The same observation holds for other metal/NH₃ HREELS studies [8,9,12]. However, in a recent study by Fisher and Mitchell [7] on the Ni(110)/NH₃ system the N–H stretch loss intensity is of almost the same magnitude as the deformation losses. And though the intensities do not, the frequencies reported by Fisher and Mitchell [7] do agree very well with those of the present study. As loss peak intensities may vary with the beam energy, we varied the latter in the range 1–10 eV, but did not observe marked changes of the relative loss peak intensity. So that at present no explanation can be given for the apparent difference of the N–H stretch losses.

The frequencies observed for condensed ammonia, see fig. 1f and table 1, are similar to those reported for other NH₃/metal systems in the high coverage region, $\theta \approx 1$ monolayer. This is expected as under these conditions the incoming electron beam probes many NH₃ molecules which are in contact with other NH₃ molecules and do not sense the presence of the Ni surface. The fact that even for submonolayer coverage the vibration frequencies observed for NH₃/Ni(110) are similar to those measured at other ammonia/metal systems and in addition not far away from the gaseous NH₃ frequencies, is compatible with the assumption of weak metal/NH₃ coupling, its adsorption energy being only ~ 15 kcal/mol.

To follow ammonia desorption in situ, HREELS spectra were recorded at increasing temperatures, starting with a monolayer formed at 186 K. As seen from fig. 2, at 300 K only the δ_s mode still can be seen, at 493 K a clean surface spectrum is recorded. It follows that NH₃ desorption is faster than

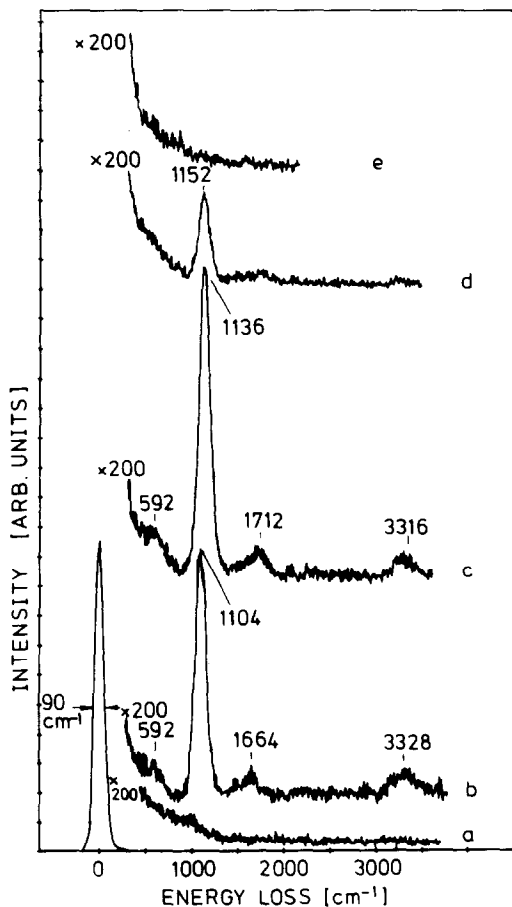


Fig. 2. HREEL spectra measured after saturating a clean Ni(110) surface (a) with ammonia at 186 K (b) and raising the temperature to 245 K (c), 300 K (d) and 493 K (e). Spectra recorded at the specified temperatures, ammonia background pressure $\leq 2 \times 10^{-9}$ Torr.

NH_3 decomposition, as otherwise spectrum e in fig. 2 should contain the fragments spectral features. We note in passing that the technique used here to record HREEL spectra at elevated temperatures does not affect the quality of the spectra: the spectra displayed in fig. 2 have been recorded at a sample which was cooled by LN_2 and heated by electric current simultaneously in order to cover the temperature range 110–500 K.

3.2. Adsorption of NH_3 at intermediate temperatures ($300 < T < 400$ K)

3.2.1. TDS results

Fig. 3 shows hydrogen (mass 2) thermal desorption spectra for a Ni(110) surface dosed with 30 L of NH_3 at different temperatures. The TD spectra for

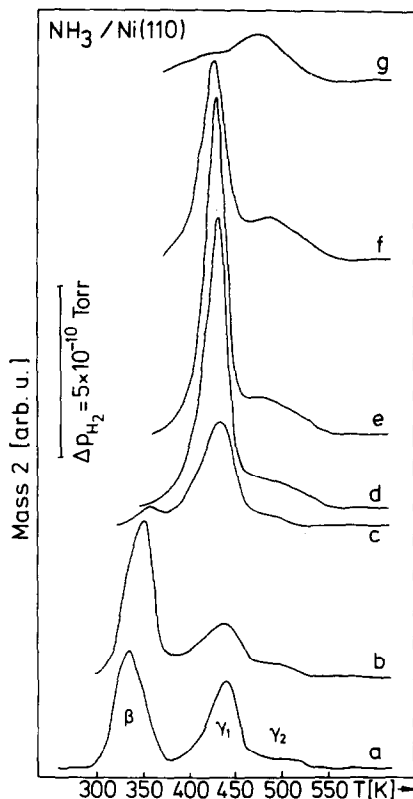


Fig. 3. Mass 2 thermal desorption spectra obtained after exposing a clean $\text{Ni}(110)$ surface to 30 L of ammonia at various temperatures: (a) 217 K, (b) 296 K, (c) 328 K, (d) 345 K, (e) 357 K, (f) 370 K and (g) 393 K.

adsorption at 217 K show three desorption states β (340 K), γ_1 (435 K) and γ_2 (480 K). The β peak is attributed to hydrogen desorption from two different processes: desorption of adsorbed hydrogen from the background and loss on one hydrogen from NH_3 . The γ_1 peak is attributed according to our EELS data as signaling the decomposition of the NH_2 species. The γ_2 peak signals the decomposition of the NH fragment.

As the adsorption temperature is increased to 328 K the β peak disappears due to thermal desorption of hydrogen at these high temperatures. See the inset in fig. 4 for a mass 2 desorption spectrum recorded after dosing clean $\text{Ni}(110)$ at 186 K with 3 L H_2 . The total amount of hydrogen evolved from the γ_1 state decreases from 217 to 296 K and increases from 328 to 357 K and decreases again at the higher temperatures. The total amount of H_2 evolved from the γ_2 state increases from 217 to 357 K and then remains fairly

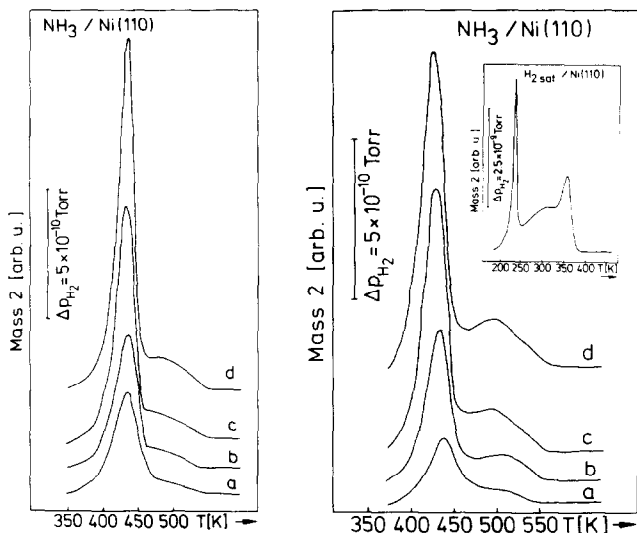
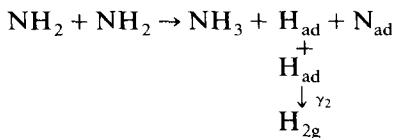


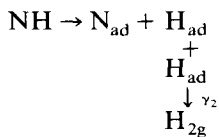
Fig. 4. Mass 2 thermal desorption spectra obtained after dosing (a) 6 L, (b) 12 L, (c) 30 L and (d) 60 L of ammonia onto a clean Ni(110) surface at 344 K (left) and 369 K (right), respectively. The inset documents a "reference" hydrogen desorption spectrum recorded after exposing 3 L of H_2 to a clean Ni(110) surface at 186 K.

constant. The ratio of γ_1 to γ_2 is approximately constant up to 357 K and at the higher temperatures the amount evolved from the γ_2 state remains constant.

Yates and coworkers [4] measured hydrogen desorption spectra after electron beam induced ammonia decomposition at low temperatures and found similar desorption spectra. The β and the γ_1 desorption peaks were assigned as in the present work, the γ_2 peak, however, was thought to be caused by a disproportionation reaction via



From the HREELS data to be presented in the next section, the origin of the γ_2 peak can be conclusively traced back to



This decomposition step only leaves N_{ad} on the surface which is observed to

desorb via a recombination step at ~ 800 K. It has been reported [13] that the NH decomposition step occurs at a much higher temperature, 800 K, signaled by almost parallel H₂ and N₂ desorption. In the present work this could not be reproduced: around 800 K only N₂ desorption (mass 28) was detected. It is believed that the mass 2 desorption peak reported previously is an ion pump induced artifact, which is absent in a turbomolecular pumped system.

From fig. 3 it can be seen that pronounced NH₂ formation starts only above ~ 300 K. As no ammonia fragmentation has been observed at low temperatures, the $\gamma_{1,2}$ desorption peaks seen in traces a and b of fig. 3 have to be caused by decomposition events which occur during the thermal desorption experiment. The increase of NH₂ coverage between 328 and 357 K, traces c, d and e in fig. 3, signals an enhanced reactive sticking coefficient, which demonstrates that at small NH₃ coverages the increase of the NH₃ surface residence time due to a larger adsorption energy causes the decomposition probability also to increase. At 370 and 393 K, traces f and g in fig. 3, the NH₂ coverage decreases. At these temperatures NH₂ already decomposes during the adsorption experiment.

Up to 357 K the ratio of integrated TD peak areas, γ_2/γ_1 , is constant at a value of ~ 0.2 . This shows that a major part of adsorbed NH₂ decomposes into N and H. Moreover, from this TDS data alone it cannot be excluded that NH originates from NH₃ decomposition without participation of NH₂. The amount of fragments accumulated at the surface depends on ammonia exposure. This is shown for two adsorption temperatures, 344 and 369 K, in fig. 4.

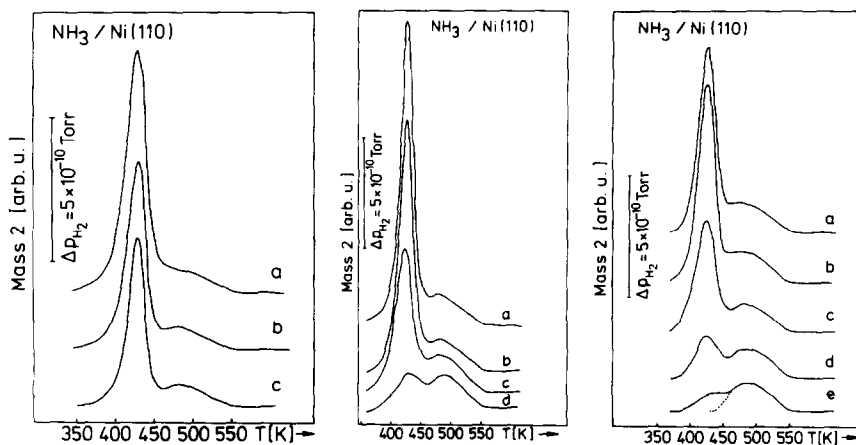


Fig. 5. Family of mass 2 thermal desorption spectra demonstrating the effects of crystal temperature and time elapsed after dosing clean Ni(110) surfaces with 30 L of ammonia. Left: adsorption temperature $T_{\text{ads}} = 345$ K, elapsed time t_e between dosing and TDS run: 2 min (a), 8 min (b), 30 min (c). Middle: $T_{\text{ads}} = 357$ K, $t_e = 4$ min (a), 8 min (b), 16 min (c), 32 min (d). Right: $T_{\text{ads}} = 369$ K, $t_e = 1$ min (a), 2 min (b), 4 min (c), 8 min (d), 16 min (e).

Using the reference hydrogen desorption spectrum, inset in fig. 4, which is known to correspond to desorption of 1.5 monolayers [11] for calibration, at $T = 344$ K after 72 L exposure of ammonia the following coverages are obtained: $\theta_{\text{NH}} = 0.1$ and $\theta_{\text{NH}_2} = 0.26$ (NH originates from NH_2 , NH_2 decomposes into NH, N and H) or $\theta_{\text{NH}_2} = 0.2$ (NH originates from NH_3 , NH_2 decomposes into N and H). Yates and coworkers [4] report $\theta_{\text{NH}_2} = 0.15$ if thermally induced ammonia fragmentation is used.

The thermal desorption spectra given in ref. [4] can be used to calculate NH and NH_2 coverages obtained by decomposing NH_3 at low temperature with an electron beam. From this data we calculate $\gamma_1/\gamma_2 \approx 5$ up to an integrated electron flux of $\sim 2 \times 10^{19}$ electrons/ m^2 . This number compares very well with that following from figs. 3 and 4 for thermal decomposition of ammonia. However, at large electron flux, $\sim 7 \times 10^{19}$ e/ m^2 , that ratio drops to ~ 3 , suggesting that even NH_2 may be fragmented by the electron beam.

The kinetics of NH_2 decomposition has been measured by recording mass 2 desorption spectra after specific time intervals elapsed after an adsorption run.

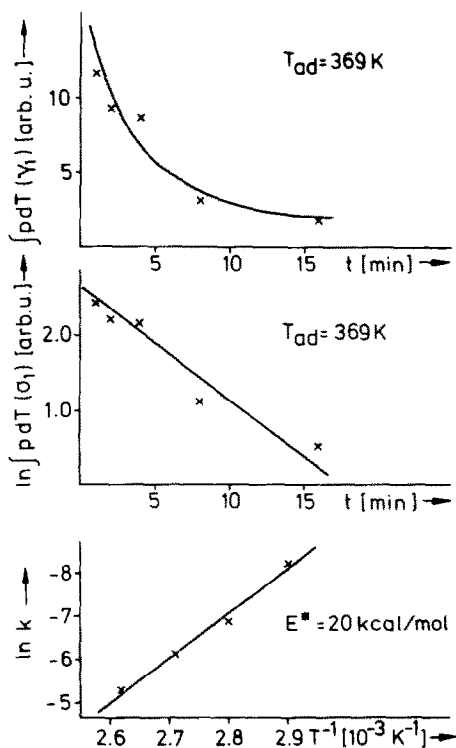


Fig. 6. Kinetics of the NH_2 decomposition reaction as evaluated from data shown in fig. 5. Linear (top) and semilogarithmic (middle) plot of the NH_2 decomposition related γ_1 -peak area, and first-order kinetics $\ln k$ versus $1/T$ plot (bottom).

Representative spectra for three temperatures, 345, 357 and 369 K, are shown in fig. 5. Plots of γ_1 versus t , see fig. 6, top, signal exponential decay of the intermediate concentration. From these curves the NH₂ decomposition activation energy is determined to $E^* = 20$ kcal/mol, see fig. 6, bottom.

3.2.2. HREELS results

In this section we present the spectroscopic justification for the interpretation of the TDS data of the previous section. Spectra b–d in fig. 7 have been recorded at 344 K, with an ambient ammonia pressure of 2×10^{-8} Torr. Spectrum a was measured before the ammonia was introduced. It is seen from this sequence that 4 loss peaks develop with time. After 45 min, corresponding to a cumulative exposure of 54 L, these peaks are at 504, 1184, 1520 and 3280

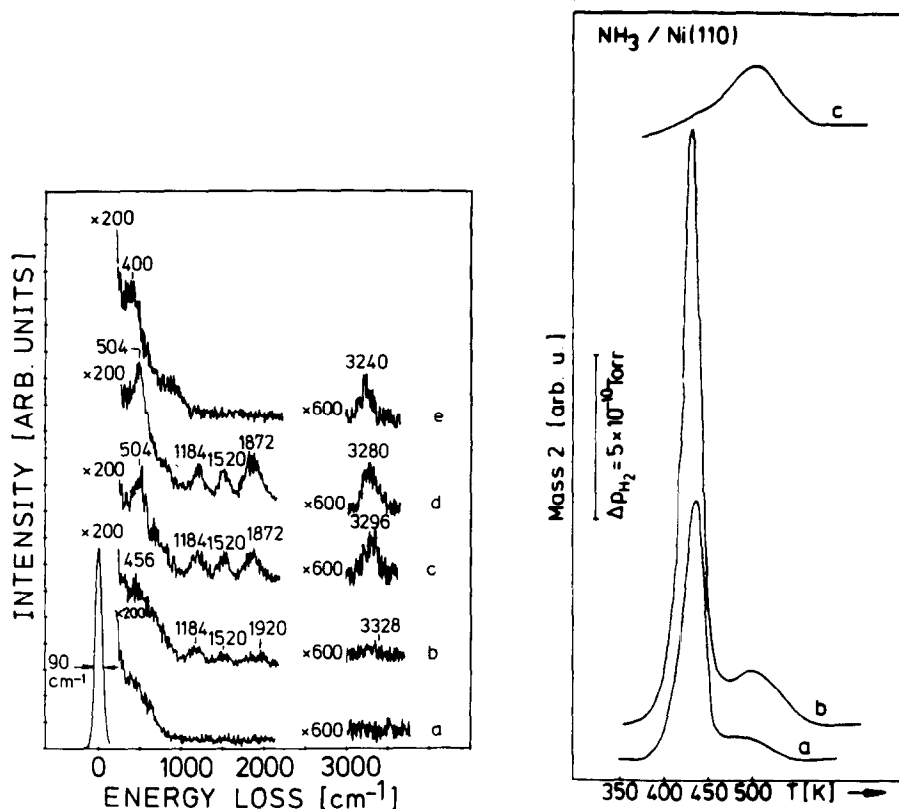


Fig. 7. Left: HREEL spectra measured (a) prior to and after establishing a 2×10^{-8} Torr ammonia partial pressure, (b) after 15 min, (c) after 30 min, (d) after 45 min at 344 K. Spectrum (e) was recorded at 393 K after (d) was completed. Right: TD spectra (mass 2) corresponding to surface conditions characterized by these HREELS spectra: HREELS b – TDS a; HREELS d – TDS b; HREELS e – TDS c.

Table 2
Group frequencies of NH_2 (in cm^{-1}) bonded to surfaces and in complexes

Mode	System		NH_2 -radical ^{a)}	$\text{C}_{60}(\text{NH}_2)(\text{NH}_3)_{10}^{5+}$ ^{b)}	$[\text{ReO}(\text{NH}_2)_4]_n$ ^{c)}	$\text{Re}_5\text{Cl}_6(\text{NH}_2)_3(\text{NH}_3)_3$ ^{c)}
	$\text{NH}_3/\text{Fe-SiO}_2$	$\text{NH}_3/\text{Na-cluster}$ ^{a)}				
$\nu_d(\text{NH})$	3380	3380				3380
$\nu_s(\text{NH})$	3290	3280	3220		3100	3226
$\delta_s(\text{HNH})$	1610	1540	1499	1560	1605	1573
$\nu(\text{Me-N})$		550		542	500	564
Technique	IR	SERS	IR	IR	IR	IR
Source	[14]	[15]	[16]	[17]	[18]	[19]

^{a)} In Ar matrix.

^{b)} NH_2 bridge bonded.

^{c)} NH_2 end on bonded.

cm⁻¹ respectively. The peak at 1872 cm⁻¹ is due to $\nu(\text{C-O})$, shifted by the presence of coadsorbed ammonia as mentioned above. Accordingly, the 1180 cm⁻¹ loss peak signals molecularly adsorbed ammonia.

By comparison with trace b in fig. 1 it is clear that the small intensity of the NH₃ δ_s makes the detection of other ammonia related loss peaks impossible. In particular, the loss peak at 3280 cm⁻¹ cannot possibly be of such intensity at such a small ammonia coverage.

The remaining three losses then are due to adsorbed NH₂ and identified as follows:

$$\nu(\text{Ni-N}): 504 \text{ cm}^{-1}, \quad \delta_s(\text{HNH}): 1520 \text{ cm}^{-1}, \quad \nu_s(\text{NH}): 3280 \text{ cm}^{-1}.$$

These numbers compare very well with those observed at NH₂ bonded to other metal surfaces or in complexes, see table 2.

If the NH₂ adsorption complex exhibits C_{2v} symmetry, the vibrations proposed above are dipole allowed, the degenerate mode $\nu_d(\text{NH})$ of NH₂ could only be excited by impact scattering [20]. The width of the 3280 cm⁻¹ loss peak may be a hint that ν_s and ν_d both contribute. Angular dependent loss spectra could help to clarify this; however, the small loss intensities render that a difficult task.

The most intense loss, the Ni-N vibration at 504 cm⁻¹, is clearly at a different frequency than the Ni-C(CO), Ni-N(N) and Ni-N(NH₃) vibrations, which are found at ~ 430, ~ 370 and ~ 450 cm⁻¹ in separate measurements. It correlates with a strong Ni-N bond and sheds some light on the Ni-NH₂ bonding geometry. According to Yates and coworkers [4] the most probable adsorption site is a "valley atop" site. This coordination allows σ donation through the doubly occupied N σ orbital and backdonation into the empty Np, in fact resulting in a strong Ni-N bond.

The intensity of the scissoring mode of NH₂ at 1520 cm⁻¹ is very small. The same is observed for the δ_s mode of adsorbed H₂O at various metal surfaces [21–24]. We have performed H₂O adsorption measurements at various temperatures and can exclude water or water fragments from being responsible for any loss structures in fig. 7.

After raising the temperature to 393 K all losses in the range 1000–2000 cm⁻¹ disappear, see fig. 7, spectrum c. At that temperature the coverages of CO and NH₃ are too small to result in detectable spectral features. More importantly, the disappearance of the NH₂ scissoring mode δ_s at 1520 signals that NH₂ no longer covers the surface. However, the loss peak at 3240 cm⁻¹ demonstrates that still NH vibrations can be excited which must be due to adsorbed NH. In the low frequency region, below 1000 cm⁻¹, a broad loss structure around 400 cm⁻¹ is seen. Most of its intensity stems from adsorbed N atoms, but if the $\nu(\text{Ni-N})$ of NH contributes to that peak it is significantly shifted with respect to the $\nu(\text{Ni-N})$ vibration of NH₂.

Table 3
Group frequencies of NH (in cm⁻¹)

System	$\nu(\text{NH})$	$\delta(\text{NH})$	$\nu(\text{M-N})$	Source
(H ₂ O) ₅ Ru-NH-Cr(H ₂ O) ₅ ⁵⁺	3200 s	1410 w		[25]
Os ₂ (NH)bipy ₄ Cl ₂ (ClO ₄) ₂	2994	1414		[17]
L ₂ Mo(O)(NH)MoL ₂	3365			[26]
Mo(NH)Cl ₂ L ₂	3300–3400			[27]
NH/Ni(111)	3340 s	1270 w	620	[28]
NH/Ni(110)	3240		(400)	Present work

s = strong, w = weak.

As there is no ν_a mode of NH, it is expected that the loss peak due to the N–H vibration for NH is narrower than for NH₂. This is in fact observed. As the intensities of the N–H vibration losses in fig. 7, spectra d and e, are of similar magnitude, although the respective coverages of the relevant species differ, it is concluded that the NH vibration excitation cross section is larger for NH than for NH₂.

In order to make TDS and HREELS experiments as supplementary as possible, TDS runs have been performed at various stages corresponding to the HREEL spectra shown in fig. 7. The right-hand-panel of fig. 7 displays mass 2 TD spectra measured in the HREELS position of the sample. Spectrum a corresponds to HREEL spectrum b, spectrum b corresponds to HREEL spectra c/d, spectrum c was measured after HREEL spectrum e was completed. These TDS data are obviously consistent with an increase of NH₂ concentration upon continuous dosing of the surface with NH₃ at 344 K as also seen in the loss spectra. In addition the γ_2 peak in spectrum c signals the decomposition of that NH which was detected by HREEL spectrum e. Note that trace c, as expected, does not exhibit desorption from NH₂ decomposition events.

The frequencies observed presently for adsorbed NH are compared in table 3 with those reported for NH in clusters and at Ni(111). As in the present case, the $\nu(\text{N-H})$ vibration is a strong band in two studies, the δ mode is weak and not seen at Ni(110). It cannot be excluded that its absence in the present study is due to an NH standing upright as has been proposed for Ni(111) [28].

From our TDS experiments it was not possible to conclude whether NH is formed from NH₃ directly or from NH₂. In order to shed some light on this problem, a surface was dosed with ammonia at 344 K and then heated to 369 K. HREEL spectra measured after these procedures are shown in fig. 8. The spectral features seen in traces b and c again signal the presence of NH₂ and NH, respectively. However, taking the strength of the $\nu(\text{N-H})$ mode of NH into account, it seems unlikely that the loss at 3288 cm⁻¹ in spectrum b

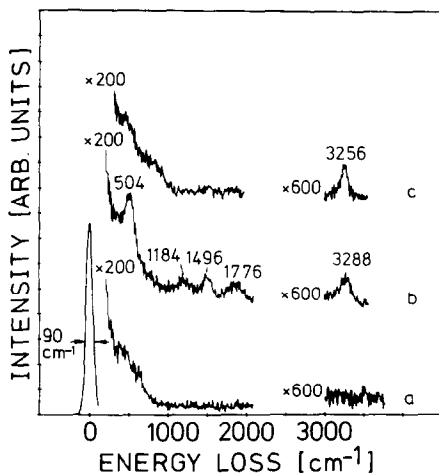


Fig. 8. HREEL spectra of a clean Ni(110) surface (a) and (b) after dosing 90 L of ammonia at 344 K. Spectrum (c) was measured after raising the temperature to 369 K.

contains NH related loss intensity. From this experiment we conclude that NH originates from decomposed NH_2 .

3.3. Electron bombardment induced fragmentation of NH_3

It has been shown that NH_3 adsorbed at metal surfaces decomposes when subjected to electron bombardment. The recent study of Yates and coworkers [4] utilizes this technique to activate ammonia fragmentation. In order to enable close connection with that work, in fig. 9 we compare HREEL spectra obtained with and without electron bombardment induced effects. After dosing a clean surface with 1 L of ammonia only molecular NH_3 related features are present (left, trace a). At elevated temperatures all these features are reduced, until at 393 K a clean surface spectrum is recorded. Note that in spectrum c a small CO related loss peak is present; however, at 393 K it is no longer present. A completely different behaviour was seen when the surface exposed to 1 L of NH_3 was subsequently irradiated with electrons, 600 eV beam energy, $\sim 10^{16}$ e/cm² integrated beam flux.

The low T spectrum exhibits a prominent CO related peak due to the increase of CO partial pressure upon operation of the LEED gun, all ammonia related loss peaks are reduced as compared with the former measurement. However, at elevated temperatures now NH_2 and NH related spectral features occur which clearly demonstrate electron bombardment induced fragmentation. Size and position of the $\nu(\text{NH})$ peak in trace b suggests that a considerable amount of NH is present at the surface, which could not be the case if

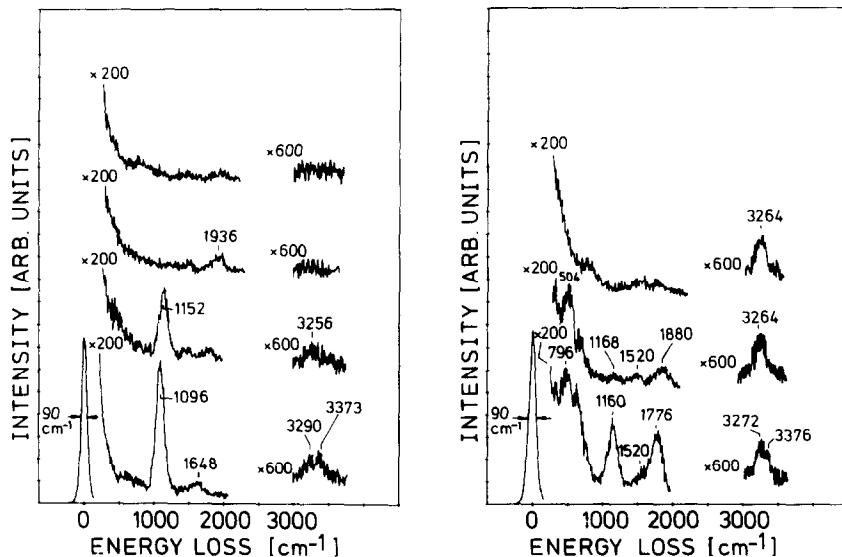


Fig. 9. Family of HREEL spectra measured after exposing 1 L of ammonia to clean Ni(110) at 186 K and subsequently raising the temperature. Left: (spectra recorded without subjecting the ammonia covered surface to a high energy electron beam) (a) 186 K, (b) 298 K, (c) 344 K, (d) 393 K. Right: (after ammonia exposure a 600 eV electron beam of an integrated flux of 10^{16} e/cm² was exposed to the surface at 186 K) (a) 186 K, (b) 344 K, (c) 369 K.

ammonia would have been decomposed by thermal activation. This finding is in complete agreement with the data discussed in section 3.2.1.

3.4. Interaction with ammonia at high temperature, $T > 400$ K

If the surface was subjected to high (10–200 L) exposures of ammonia in the range 400–550 K, a well defined 2×3 LEED pattern was observed and a prominent N_2 (mass 14) TD peak was measured in subsequent thermal desorption spectra. Loss spectra gave no hint of the existence of molecular species after exposing the surface to ammonia at those high temperatures, as illustrated in fig. 10. Only a small shoulder near the elastic peak is indicative of the nitrogen atoms now present on the surface.

Subjecting this surface to treatment at even higher temperature caused loss peaks to occur in the molecular frequency region, ~ 880 and 1520 cm⁻¹. Auger spectra revealed only C and N as non Ni-related elemental surface species. After flashing the sample to 890 K, which removed adsorbed N by associative desorption of N_2 , only C was left at the surface and the loss peak at 1520 cm⁻¹ had vanished (trace d, fig. 10). Even after subsequent flashing to 1000 K the feature at 880 cm⁻¹ persisted, as was observed with the C Auger

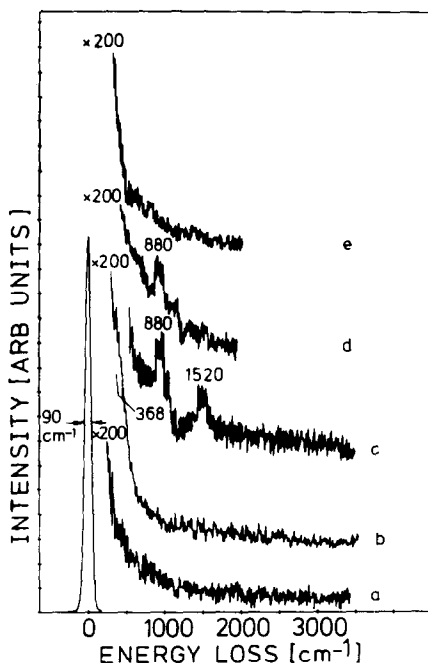


Fig. 10. HREEL spectra corresponding to (a) clean Ni(110) at 493 K; (b) after 50 L ammonia exposure at 493 K; (c) as (b) at 662 K; (d) as (b), flashed to 891 K, measured at 662 K; (e) after sputtering.

peak, and could only be removed by subjecting the surface to Ar^+ or oxygen treatment. This then caused the C Auger peak to disappear and enabled “clean surface” related H_2 desorption spectra to be recorded as shown in fig. 4, inset. Loss spectra as shown in fig. 10, traces c and d, have often been observed in this study when large quantities of NH_3 had been dosed to the surface.

Auger spectra suggest us to connect the loss around 1520 cm^{-1} with C and N, and the loss around 880 cm^{-1} with C, respectively. Both peaks are in a frequency range where C–N and C–Met are logical candidates. Cyano groups have been observed at Pt, Cu, Ru and Ni surfaces after C_2N_2 or HCN adsorption. Associative N_2 desorption is reported to occur in the range 650–900 K [29,30], leaving carbon back at the surface. With Ni(111) it is assumed that C–N is bonded side-on to the surface [30]. A vibrational spectroscopy study of CN group bonded side-on to Ni atoms is reported for t-butyl-isonitril attached to a Ni_4 cluster in tetrahedral geometry [31]. In this case the $\nu(\text{CN})$ is located at 1605 cm^{-1} , considerably reduced with respect to the gas phase value, 2089 cm^{-1} for HCN. 1605 cm^{-1} compares very well with the value observed here, 1520 cm^{-1} .

C–Met vibrations in the frequency range in question, 900 cm^{-1} , have been reported for C at $\text{Ru}(001)$ [32], Met–C diatomics exhibit frequencies at $\sim 1000\text{ cm}^{-1}$ [33], at $\text{Fe}(111)$ a carbon induced loss peak at 1290 cm^{-1} has been related with on-top bonded C [34]. According to these findings we interpret the loss at 880 cm^{-1} as originating from top site bonded carbon.

3.5. NH_3 decomposition at oxygen covered surfaces

The large electron affinity of oxygen makes this atom a candidate to promote metal/molecule bonding and fragmentation when electron donation mechanisms are involved. Accordingly, it has been found at various metal surfaces, e.g. $\text{Ni}(110)$ [3], $\text{Ni}(100)$ [35] and others [36–38], that the ammonia adsorption energy increases. In addition, the ammonia decomposition rate has been observed to increase at Cu [39] and Ni [3].

Besides that, a structural effect, namely azimuthal ordering of NH_3 in the presence of coadsorbed oxygen, has been concluded to operate from ESDIAD studies at the $\text{Ru}(001)/\text{NH}_3$ [38] and $\text{Ni}(111)/\text{NH}_3$ [37] systems.

Oxygen induced effects in the present work have only been studied with respect to the decomposition related aspects, no attempt has been made to study the system $\text{Ni}(110)/\text{O}/\text{NH}_3$ thoroughly. As the oxygen covered surface is known to exhibit structural changes when subjected to temperature changes [40], the $\text{Ni}(110)$ surfaces have been flashed to 493 K subsequent to oxygen deposition.

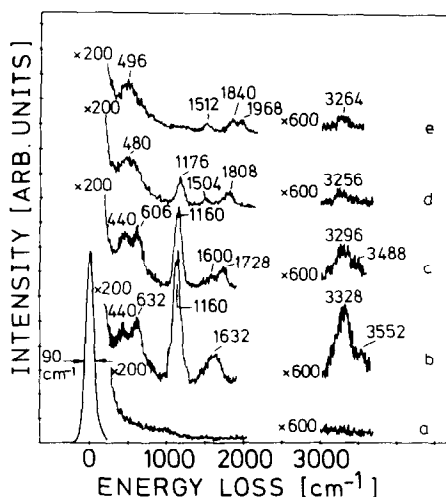


Fig. 11. HREEL spectra illustrating the promoting effect of oxygen on the ammonia decomposition reaction: (a) clean surface at 186 K ; (b) after 0.1 L oxygen exposure with subsequent anneal at 493 K and 2 L ammonia exposure at 186 K , spectrum recorded at 186 K ; after raising the temperature to (c) 245 K , (d) 296 K , (e) 345 K .

Fig. 11 displays a family of HREEL spectra obtained after dosing an oxygen precovered surface with 2 L of ammonia. At low temperature loss peaks at 440, 632, 1160, 1632, 3328 and 3552 cm^{-1} are observed. As the oxygen coverage is too small to be responsible for a Ni–O vibration related loss peak, the structure at 440 cm^{-1} is interpreted as being due to the Ni–N vibration, shifted with respect to the case without oxygen coadsorbate ($\sim 350 \text{ cm}^{-1}$) as the metal/molecule bond became stronger.

Loss peaks at 632, 1160 and 1632 cm^{-1} are connected with the ρ_r , δ_s and δ_d modes of ammonia, respectively. Comparing these numbers with those observed under comparable coverage conditions at $\text{Ni}(110)/\text{NH}_3$, the shift of the δ_s mode is most pronounced: from 1104 to 1160 cm^{-1} . This is caused by increased donative bond and has been earlier observed and discussed for the $\text{Cu}(110)/\text{O}/\text{NH}_3$ system [9]. Most prominent is the large intensity in the $\nu(\text{NH})$ region around 3328 cm^{-1} . This may be either due to an enhanced scattering probability under the given coadsorbate conditions, or just due to the fact that already NH_3 had partially decomposed at that temperature. The shoulder at 3552 cm^{-1} , trace b, fig. 11, is identified as originating from $\nu(\text{OH})$ [44], just as the feature at 3560 cm^{-1} seen in the $\text{Cu}/\text{O}/\text{NH}_3$ study [9].

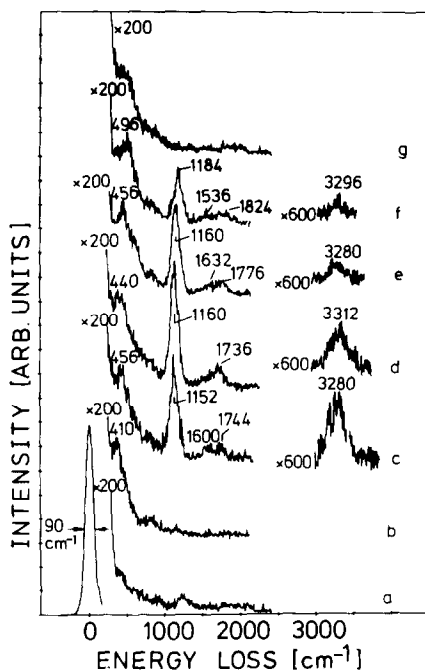


Fig. 12. HREEL spectra corresponding to (a) clean $\text{Ni}(110)$ at 110 K; (b) 0.3 L oxygen exposure, anneal at 493 K; (c) subsequent 5 L exposure at 110 K; after raising the temperature to (d) 186 K, (e) 245 K, (f) 300 K, (g) 344 K.

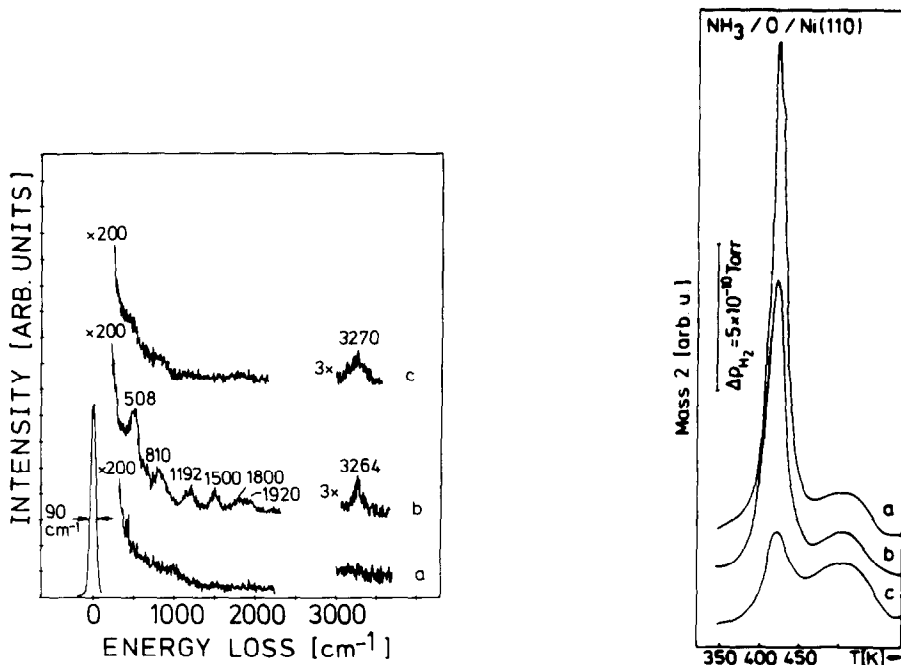


Fig. 13. Left: HREEL spectra recorded at a Ni(110) surface predosed with 0.15 L of oxygen and subsequently exposed to ammonia at 344 K (a) prior to the installation of a fixed ammonia pressure, $p = 2 \times 10^{-8}$ Torr; (b) after 15 min; (c) after 60 min. Right: corresponding TD (mass 2) spectra: 0.15 L oxygen predosed, 30 L ammonia dosed at 344 K (a) after 2 min, (b) 30 min, (c) 60 min.

Upon increasing the temperature to 345 K, the presence of NH_2 fragments can be concluded from the losses at 496 cm^{-1} ($\nu(\text{Ni-N})$), 1512 cm^{-1} ($\delta(\text{H-NH})$) and 3264 cm^{-1} ($\nu(\text{N-H})$). As in previous runs, CO is the major contamination. Comparing with the results obtained without oxygen coadsorbate at low temperature NH_3 -exposed Ni(110) surface, obviously the balance between the competitive desorption and decomposition reactions has changed: decomposition is favoured by oxygen as the NH_3 adsorption energy is increased due to the presence of the coadsorbate.

At higher oxygen precoverage, see fig. 12, the promoting effect is even more pronounced. The $\nu(\text{Ni-N})$ vibration at 496 cm^{-1} is detected already at 300 K, at 344 K no NH_2 species remains. This suggests that the decomposition of NH_2 , too, is enhanced by oxygen.

This conclusion is confirmed by combined HREELS/TDS data shown in fig. 13. A Ni(110) surface was dosed with 0.15 L of oxygen and annealed as stated above. Subsequently, loss spectra were recorded at 344 K and ambient NH_3 (2×10^{-8} Torr) pressure. After 15 min NH_2 is clearly detected by the

δ (HNN) vibration, after 60 min only NH is left. Note that under these conditions without O_{ad} , NH_2 has proven stable. Mass 2 desorption spectra accordingly at 344 K signal NH_2 decomposition by a decrease of the γ_1 peak.

4. Conclusions

NH_3 , NH_2 and NH species adsorbed on a Ni(110) surface were identified by means of their vibrational spectra in combination with thermal desorption spectroscopy. The frequencies of various vibrational modes of these three species compare well with the data for other metal surfaces or transition metal complexes.

Exposure of the surface to ammonia at $T < 190$ K leads to non-dissociative NH_3 adsorption followed by multilayer formation. Upon raising the temperature the adsorbed NH_3 partly desorbs with an activation energy of around 15 kcal/mol, and partly dissociates into its NH_2 and NH fragments. The activation energies for the latter processes are presumably higher than that for NH_3 desorption, since the NH_2 and NH species are formed in larger concentrations only if the surface is exposed to NH_3 at $T > 300$ K. These species decompose further into $N_{ad} + H_{ad}$ at even higher temperatures, whereby the activation energy for NH_2 decomposition was determined to be 20 kcal/mol.

The ranges of thermal stability of the various surface species are comparable with those observed with Fe surfaces [41]. The inability of nickel to catalyse synthesis of ammonia from the elements is therefore most probable due to the extremely low sticking probability for the first step, namely dissociative nitrogen adsorption [42].

Acknowledgements

ICB is grateful to the Alexander von Humboldt-Stiftung who granted a fellowship. Further financial support was obtained from the Deutsche Forschungsgemeinschaft (SFB 128).

References

- [1] M. Grunze, M. Golze, R.K. Driscoll and P.A. Dowben, *J. Vacuum Sci. Technol.* 18 (1981) 611.
- [2] K. Jacobi, E.S. Jensen, T.N. Rhodin and R.P. Merrill, *Surface Sci.* 108 (1981) 397.
- [3] T.E. Madey and C. Benndorf, *Surface Sci.* 152/153 (1985) 587.
- [4] C. Klauber, M.D. Alvey and J.T. Yates, Jr., *Surface Sci.* 154 (1985) 139.
- [5] U. Seip, M.-C. Tsai, K. Christmann, J. Küppers and G. Ertl, *Surface Sci.* 139 (1984) 29.
- [6] V. Penka, Doctoral Thesis, Munich (1985).

- [7] G.B. Fisher and G.E. Mitchell, *J. Electron Spectrosc. Related Phenomena* 29 (1983) 253.
- [8] B.A. Sexton and G.E. Mitchell, *Surface Sci.* 99 (1980) 523.
- [9] D. Lackey, M. Surman and D.A. King, *Vacuum Technol. Appl. Ion Phys.* 33 (1983) 867.
- [10] W. Erley and H. Ibach, *Surface Sci.* 119 (1982) L357.
- [11] K. Christmann, V. Penka, R.J. Behm, F. Chehab and G. Ertl, *Solid State Commun.*, to be published.
- [12] J.L. Gland, B.A. Sexton and G.E. Mitchell, *Surface Sci.* 115 (1982) 623.
- [13] M. Hüttinger and J. Küppers, *Surface Sci.* 130 (1983) L277.
- [14] T. Nakata and S. Matsushita, *J. Phys. Chem.* 72 (1968) 458.
- [15] W. Schulze, B. Breithaupt, F. Frank and F.W. Froben, *Surface Sci.* 156 (1985) 963.
- [16] D.E. Milligan and M.E. Jacox, *J. Chem. Phys.* 43 (1965) 4487.
- [17] D.J. Hewkin and W.P. Griffith, *J. Chem. Soc. A* (1966) 472.
- [18] D.A. Edwards and R.T. Ward, *J. Chem. Soc. Dalton* (1972) 89.
- [19] D.A. Edwards and R.T. Ward, *J. Inorg. Nucl. Chem.* 35 (1973) 1043.
- [20] B.A. Sexton and G.E. Mitchell, *Surface Sci.* 99 (1980) 539.
- [21] H. Ibach and S. Lehwald, *Surface Sci.* 91 (1980) 187.
- [22] P.A. Thiel, F.M. Hoffmann and W.H. Weinberg, *J. Chem. Phys.* 75 (1981) 5556.
- [23] E.M. Stuve, S.W. Jorgenson and R.J. Madix, *Surface Sci.* 146 (1984) 179.
- [24] B.A. Sexton, *Surface Sci.* 94 (1980) 435.
- [25] R.P. Cheney and J.N. Armor, *Inorg. Chem.* 16 (1977) 3338.
- [26] A.W. Edelblut, B.L. Haymore and R.A.D. Wentworth, *J. Am. Chem. Soc.* 100 (1978) 2250.
- [27] J. Chatt and J.R. Dilworth, *J. Chem. Soc. Chem. Commun.* (1975) 983.
- [28] J.L. Gland, G.B. Fisher and G.E. Mitchell, preprint.
- [29] N.J. Gudde and R.M. Lambert, *Surface Sci.* 124 (1983) 372.
- [30] J.C. Hemminger, E.L. Muetterties and G.A. Somorjai, *J. Am. Chem. Soc.* 101 (1979) 62.
- [31] V.W. Day, R.O. Day, J.S. Kristoff, F.J. Hirsekorn and E.L. Muetterties, *J. Am. Chem. Soc.* 97 (1975) 2571.
- [32] M.A. Barteau, J.Q. Broughton and D. Menzel, *Appl. Surface Sci.* 19 (1984) 92.
- [33] K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. 4. Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).
- [34] U. Seip, M.-C. Tsai, J. Küppers and G. Ertl, *Surface Sci.* 147 (1984) 65.
- [35] M. Grunze, P.A. Dowben and C.R. Brundle, *Surface Sci.* 128 (1983) 311.
- [36] M. Grunze, C.R. Brundle and D. Tomanek, *Surface Sci.* 119 (1982) 133.
- [37] F.P. Netzer and T.E. Madey, *Surface Sci.* 119 (1982) 422.
- [38] C. Benndorf and T.E. Madey, *Chem. Phys. Letters* 101 (1983) 59.
- [39] C.T. Au and M.W. Roberts, *Chem. Phys. Letters* 74 (1980) 472.
- [40] J. Wintterlin, *Diploma Thesis, Munich* (1985).
- [41] G. Ertl, *J. Vacuum Sci. Technol.* A1 (1983) 1247.
- [42] M. Grunze, R.K. Driscoll, G.N. Burland, J.C.L. Cornish and J. Pritchard, *Surface Sci.* 89 (1979) 381.
- [43] P. Hollins, J. Pritchard, B.J. Bandy, N.D.S. Canning, M.A. Chesters and N. Sheppard, *Vacuum Technol. Appl. Ion Phys.* 33 (1983) 877.
- [44] K. Wagemann, *Diploma Thesis, Munich* (1985).