Adsorption and decomposition of hydrazine on Ru(001)

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The adsorption and decomposition of hydrazine on Ru(001) have been investigated in the temperature range 150-1000 K utilizing HREELS, thermal desorption and reaction spectroscopy, LEED and $\Delta \Phi$ measurements. N₂H₄ multilayers desorb in one peak at \approx 190 K. After desorption of these multilayers, a chemisorption layer consisting mainly of molecular hydrazine remains. Decomposition of monolayer hydrazine starts approximately at 220 K. The thermal evolution of this reactive chemisorption layer has been investigated in detail. N–N bond and N–H bond scission proceed essentially in parallel, with the first being complete at lower T. In monolayer TPD, the desorption products N₂, NH₃ and H₂, but not N₂H₄, are observed. In the course of the complex N₂H₄ thermal decomposition, several intermediate species can be identified in different temperature ranges, among them surface NH₂ (220...280 K) and surface NH (280... \approx 480 K). The latter is the last intermediate containing an N–H bond. The final decomposition product on the surface is atomic N for T > 480 K which desorbs recombinatively between 570 and 1000 K. The decomposition routes and reaction mechanisms leading to these intermediate and final products are discussed.

1. Introduction

Hydrazine (N_2H_4) is an important reducing agent which decomposes spontaneously above room temperature into nitrogen, hydrogen and ammonia. On metal surfaces, several pathways leading to these final products have been proposed which include the formation of surface radicals (e.g. of the form NH_x). Only in a very limited number of cases the unequivocal identification of such intermediates has been possible. The heterogeneous decomposition of hydrazine on single crystal surfaces of metals has been studied in the past by a number of investigators. There are, for example, studies on Ni(111) [1], Pt(111) [2], Pd(100) [3], Rh(111) [4], Rh(100) [5],Ir(111) [6], Ru(001) [7] and Fe(111) [8]. All these studies demonstrated that the decomposition routes are complex. In addition, the adsorption and decomposition of hydrazine has been studied on polycrystalline metal surfaces, e.g. on Rh [9,10], Al [11] and Ir [12].

Other studies on hydrazine decomposition, especially on semiconductor surfaces like $Si(111)7 \times 7$

[13], were aimed primarily at the production of surface nitride layers as an alternative to nitridation using ammonia CVD. These passivation layers are promising technological applications because of their outstanding resistance against environmental influences. In earlier work [14] with the emphasis on the production of isocyanate on Ru(001) we reported that the final (and, at temperatures above 480 K, the only) surface species resulting from decomposition of N₂H₄ on Ru(001) is also atomic nitrogen.

However, few studies deal with the detailed investigation of the N_2H_4 decomposition path on the basis of an identification of intermediate species, on transition metals. The detecting of such intermediates can yield important information about the relative stability of the N-N and the N-H bonds in hydrazine and its dissociation products on surfaces. Depending on the surface, several different primary dissociation steps for hydrazine are possible. In the first, the decomposition starts with the rupture of one or more N-H bonds, leaving fragments with an intact N-N bond. The alternative initial step is the scission of the N-N bond which produces NH_x species. A third possibility is a concerted dissociation-reaction mechanism which for example can produce ammonia in the primary decomposition step. These three decompo-

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sition mechanisms have been proposed for various surfaces. In some cases, intermediates could be identified to give positive proof of one or another dissociation step. Thus, the first alternative has been concluded to proceed on Pt(111) [2] and the second one on Fe(111) [8]; on Ni(111) Gland et al. [1] have succeeded in the first identification of surface NH on a single crystal transition metal surface.

In this paper, we report a detailed study of the adsorption and thermal decomposition of N_2H_4 on Ru(001) utilizing a combination of HREELS, TDRS, LEED and $\Delta \Phi$. We succeed in clear identification of intermediate species in the dissociation path, and derive information on the connected mechanisms on this well-defined surface.

2. Experimental

The experimental procedures have been described in an earlier paper [15]. HREELS, TPD and LEED measurements were carried out under a residual gas pressure of 6×10^{-9} Pa (5×10^{-11} mbar). The resolution of the HREELS spectrometer was $50-60 \text{ cm}^{-1}$. The loss spectra were recorded digitally with the sample at 120 K. The sampling time was 2 seconds per point. The TPD equipment consists of a quadrupole mass spectrometer (Balzers QMS 112) with Feulner cup [16] which allows to quantitatively reproduce and thus calibrate - the TPD spectra to a few percent. The heating rate used was 2.5 K s⁻¹. A Kelvin probe [17] was used to determine the work function changes after hydrazine adsorption and during heating of the coadsorbate layers. The cleaning procedure of the sample included several heating cycles (up to 1400 K) in oxygen followed by annealing to 1570 K in UHV. The cleanliness of the surface was monitored by LEED, HREELS and $\Delta \phi$ measurement during hydrogen adsorption on Ru(001) at 300 K [18].

Anhydrous hydrazine was prepared from 98% hydrazine hydrate by repeated distillation over sodium hydroxide or barium hydroxide under nitrogen, until a constant boiling point of 386.65 K had been reached. It was further purified by fractional crystallization and numerous freeze-thaw cycles under vacuum, and was stored in a darkened ampule at 2° C to prevent disproportionation. Deuterated hydrazine was obtained from MSD Isotopes. To minimize hy-

drazine decomposition, the hydrazine dosing reservoir was carefully preconditioned by long-term exposure to hydrazine prior to each experimental run. Between experiments the hydrazine in the dosing manifold was frequently replaced in order to minimize decomposition inside the dosing line which had been carefully modified to the same end (minimum possible length of line made of glass and stainless steel only, use of Au or gilded Cu gaskets only, and of special corrosion-proof valves). Decomposition of the hydrazine into NH₃, N₂ and H₂ could be detected in the mass spectra after allowing the N₂H₄ to sit overnight in the glass-stainless steel ampule. Therefore, before each dosing, additional freeze-pump cycles were performed. After this dosing procedure, the cracking pattern of the hydrazine mass spectrum was in very good agreement with the one reported in ref. [3].

Hydrazine was dosed via a stainless steel tube (diameter 6 mm) on to the crystal. It was necessary to use this dosing method, because the very large sticking coefficient of N_2H_4 in the glass capillaries of the microchannel array used for other gases (see, for example, refs. [15,19]) turned out to make an exact dosing extremely difficult because of a storage effect in the array.

3. Results and interpretation

3.1. Multilayers

Adsorption of hydrazine on Ru(001) below 170 K leads to physisorbed multilayers. Individual layers of physisorbed hydrazine cannot be resolved in TDS. Rather, the TPD spectra exhibit a single peak of molecular hydrazine, which does not saturate with increasing coverage (fig. 1). With increasing coverage, the peak maximum shifts from 185 to 189 K; the fwhm of spectrum f is 6.3 K. While the rising edges of all spectra fall together with satisfactory accuracy, all the multilayer peaks are asymmetric with strong broadening of the falling edge. This is incompatible with pure zero order desorption throughout the whole peak range and could possibly be an indication for unresolved subpeaks. However, the main cause for the broadening probably is the large sticking coefficient of hydrazine on glass and ceramic, which also

Fig. 1. TPD spectra of N_2H_4 multilayers (m/e=32). Dose: (a) 1.1 L, (b) 2.3 L, (c) 3.0 L, (d) 5.0 L, (e) 6.5 L, (f) 13 L. Heating rate 2.5 K/s.

complicated the dosing via the microchannel array: readsorption of hydrazine inside the glass cup around the ion source of the QMS will delay the partial pressure decrease after completed desorption, in particular for large desorbing amounts.

The vibrational spectra of physisorbed N_2H_4 can be compared with gaseous and crystalline hydrazine. In addition to the gas phase modes, frustrated translations and rotations (librational modes) are possible in the hydrazine crystal. These modes may also be observed in multilayers provided their thickness is sufficient.

The space group of crystalline hydrazine is P2₁ [20] with two molecules per unit cell while the molecule itself has C₂ symmetry, with the N-N bond perpendicular to the C₂ axis. Because of this low symmetry, all the infrared active modes of the gas phase should be observable in specular direction even in a relatively thin physisorbate of three to four layers, provided that their dynamical dipole moments are sufficiently large. There are 12 IR-active fundamental modes for hydrazine, seven A and five B modes. Three of them have large amplitudes and very high IR intensity in the gas phase: ν_7 (NH₂ torsion), ν_6 and ν_{12} (symmetric and antisymmetric wagging or inversion modes of the NH₂ groups) [21].

Fig. 2 shows vibrational spectra of N_2H_4 and N_2D_4 multilayers (dose 3 L at $T_{ad} = 120$ K) recorded in specular direction. The mode assignment follows from a comparison of these spectra with crystalline hydra-

Fig. 2. HREEL spectra of N₂H₄ (lower panel) and N₂D₄ (upper panel) multilayers, recorded in specular direction. Dose 5 L, $E_p=5$ eV, $T_{ad}=120$ K. Dots: data points; solid line: Fourier smooth.

zine [20,22], gas phase hydrazine [21–25] and matrix-isolated hydrazine [23,26]. In some cases, there are considerable differences of frequency values of corresponding modes between gas phase and matrixisolation; additionally, the frequencies depend on the kind of matrix (N or Ar matrix [23]). Also, the frequencies and, consequently, the mode assignments vary in several publications. For example, Giguere and Liu [22] give values between 885 and 1072 cm⁻¹ for ν_5 (N–N stretch), whereas Durig et al. report 1126 cm⁻¹ [25]. We use for gas phase hydrazine the values of Tipton et al. [23] and for crystalline hydrazine the values of Durig et al. [25] in table 1 because these seem to be the most complete and critical sources.

The four N-H stretch modes of gaseous hydrazine are not resolved in the multilayer HREEL spectra, although for N_2D_4 two bands at 2350 and 2460 cm⁻¹ can be separated (fig. 2). For N_2H_4 , these bands were not well resolved.

The loss at 1615 cm⁻¹ (1200 cm⁻¹ for N_2D_4) can





Table	1
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Normal modes of hydrazine. Abbreviations: s=symmetric, a=antisymmetric, wag=wagging, str=stretch, twi=twist, scis=scissor, PED=potential energy distribution according to ref. [23]. All values in cm⁻¹. The first of the s/a labels for the NH stretch vibrations refers to the direction of one NH_{inner} (NH_{outer}) movement relative to the other NH_{inner} (NH_{outer}) movement; the second refers to the relative motion of the two NH stretches within a given amino group. Gas phase values taken from refs. [21–24]; for crystalline hydrazine from ref. [25]

Mode No.	Irred.	Irred. Gas phase		Crystalline		Ru(001)		Approx.
	repr.	N₂H₄	N_2D_4	N₂H₄	N_2D_4	N_2H_4	N_2D_4	FED [23]
				172	156	171	≈160	libration
ν_7	Α	377	291					torsion
V6	Α	780	645	870	744	880	≈780	s-HNH-wag
ν_{12}	В	937	723	1066	814	1080	790	a-HNH-wag
Vs	Α	1098	933	1126	938	1080	≈850	N–N-str + s-HNH-wag
v ₁₁	В	1275	972	1350	1004	1230	980	a-HNH-twi
V4	Α		1009	1304	1041	1330		s-HNH-twi
ν_{10}	В	1608	1194	1655	1213	1615	1200	a-HNH-scis
V 3	Α	1493	1140	1603	1184	1615	1200	s-HNH-scis
Va	В	3297	2436	3310	2469	3290	2460	a/s-HNH-str
ν_2	Α			3200	2347	-	2350	s/s-HNH-str
ν_1	Α	3325	2542	3310	2407	3340	2350	s/a-HNH-str
ν_8	В	3350	2532	3310	2479		2460	a/a-HNH-str

clearly be attributed to the NH₂ deformation modes $(\delta$ -NH₂ or NH₂ scissor). These are the modes indicative for intact NH₂ groups, because in this frequency range these are the only NH_x modes with appreciable intensity; we will make use of this indicator below.

The NH₂ twist modes are identified at 1230–1330 cm^{-1} ; the corresponding N₂D₄ modes should be around 980 cm⁻¹. The multilayer spectra for N_2H_4 and N_2D_4 are dominated by one loss peak each $(N_2H_4: 1080 \text{ cm}^{-1}; N_2D_4: 790 \text{ cm}^{-1})$. Assignment of this peak is not straightforward. For N₂H₄, possible candidates are ν_{12} , ν_5 and, under the assumption of strong disturbance of the molecule, v_6 . For N₂D₄, these are v_6 , v_{12} and, also under the condition of strong disturbance, ν_5 . For gas phase and crystalline hydrazine, the intensity of v_{12} is at least one order of magnitude higher than for all other modes, with the exception of ν_6 with half the intensity of ν_{12} . The intensity of ν_5 is one order of magnitude smaller; note that this is no pure N-N stretch. The contribution of the NH_2 (ND_2) twist vibration has been calculated for N₂H₄ to be 17% and for N₂D₄ 59% [23]. The intensities become plausible if one takes into account that the high static dipole moment of hydrazine $(1.85-1.90 \text{ D}; 6.33 \times 10^{-30} \text{ A s m})$ is oriented perpendicular to the N–N bond because of the gauche configuration of the molecule [27]. ν_5 is essentially polarized parallel to the N–N bond while ν_{12} and ν_6 essentially induce dipole moment changes perpendicular to the N–N axis. Comparison of the N₂H₄ and the N₂D₄ data supports the interpretation that the main contribution for the 1080 cm⁻¹ (790 cm⁻¹) peak comes from ν_{12} . Certainly there are also contributions from ν_5 .

The 880 cm⁻¹ loss in N₂H₄ can be attributed to ν_6 , which in deuterated hydrazine overlaps with ν_{12} .

The NH₂ torsion mode ν_7 , which is observed in the gas phase spectra with similar intensity as ν_6 (transitions $0 \rightarrow 1$, $0 \rightarrow 2$ and $1 \rightarrow 2$ were observed in refs. [25,26]) loses one to two orders of magnitude in intensity by matrix-isolation and in the crystalline phase. Therefore it cannot be resolved very well here. This holds especially for N₂D₄ because of the overlap with a librational mode (see below).

The 495 cm⁻¹ loss in the N₂D₄ spectrum is probably due to a ν (Ru–NH_x) mode which is incompletely screened by the multilayer.

An interesting feature is the very high intensity peak at 170 cm^{-1} (N₂H₄). Varying the primary energy between 3 and 10 eV gave no indication for resonant excitation of this mode. The comparison with crystalline hydrazine [20] indicates that this loss may be due to a libration (i.e. frustrated rotation). In principle, there should be nine lattice modes for crystalline hydrazine in the range 107–275 cm⁻¹, seven of which have been identified [20]. In the N₂D₄ spectra, these lattice modes could not be resolved, maybe because of their even lower frequency. There is clearly some structure at the energy gain side in the N_2H_4 spectrum (fig. 2, lower panel) at -170 cm^{-1} , which can be attributed to an anti-Stokes-feature. At T = 115K the Boltzmann factor is $kT = 9.9 \text{ meV} (80 \text{ cm}^{-1})$. Therefore, the intensities of the Stokes and anti-Stokes line should exhibit a ratio of $exp(\hbar\omega/$ kT = 8.3. This is in good agreement with the experimental result $(I(170)/I(-170) \approx 9)$, in view of the limited resolution and the still high intensity of the elastic peak in this range.

The mode assignment thus reached is summarized in table 1; it can be used as a starting point for the adsorbate case as well. For comparison the corresponding frequency values for gaseous and crystalline hydrazine are also given.

3.2. Chemisorption layers: thermal desorption and $\Delta \Phi$

For the following experiments, hydrazine was dosed at 170 K to minimize dissociation during adsorption and to suppress the growth of multilayers. The figs. 3, 4 and 5 show TPD spectra for increasing hydrazine doses. The results indicate a high reactivity of hydrazine on Ru(001). The desorption products are N₂, H₂ and NH₃. No other desorption products like diimine (N₂H₂) were found, which is, for example, the case on polycrystalline Rh [9,10] (but not on Rh(111) [4]). In particular *no* molecular desorption of hydrazine was detectable from the chemisorption layer.

At low N₂H₄ dose there is only one H₂ peak at 405 K (α_1 ; fig. 3a), which saturates after a dose of about 0.3 L. Simultaneously, a second peak can be identified (α_2) which shifts with increasing dose from 330 to 305 K. As soon as α_2 is separable, α_1 clearly shifts to higher temperature (by about 20 K). Hydrogen which desorbs in peaks α_1 or α_2 must originate from hydrazine or its dissociation products. Because α_2 shifts with increasing fractional coverage to lower temperatures, we assume essentially second order de-



Fig. 3. TPD spectra for m/e=2 (H₂) from N₂H₄/Ru(001) at increasing hydrazine doses. Hydrogen desorption corresponding to a coverage of (in ML): (a) 0.27, (b) 0.33, (c) 0.38, (d) 0.40, (e) 0.41, (f) 0.42, (g) 0.44, (h) 0.45, (i) 0.53, (j) 0.60. $T_{ad}=170$ K, heating rate 2.5 K/s.

sorption, even though the peak shape suggests additional effects at low coverages. This suggests that α_2 is at least partially rate limited by recombinative desorption of adsorbed H atoms $(2H_{ad} \rightarrow H_{2,gas})$. The asymmetric peak shape and the relatively strong modification compared with desorption of pure H/ Ru(001) [18] may be caused by the influence of other dissociation products (for example NH_x). Additionally, other reactions may contribute, which cannot be further specified for the moment. An estimation of the desorption energy of α_2 -H₂ with the assumption of second order desorption according to Chan et al. [28] yields $E_d = 118$ kJ/mol for $T_p = 305$ K.

In contrast, α_1 is most probably limited by scission of N-H bonds, because its peak temperature is considerably above the desorption temperature of pure H/Ru(001). The shift to higher T_p in the presence of α_2 must then be a coadsorbate effect. This will be-



Fig. 4. TPD spectra for m/e=17 (NH₃) from N₂H₄/Ru(001) at increasing hydrazine doses. Ammonia desorption corresponding to a coverage of (in ML): (a) 0.02, (b) 0.04, (c) 0.07, (d) 0.20, (e) 0.21, (f) 0.22, (g) 0.27, (h) 0.28, (i) 0.29, (j) 0.30. $T_{ad}=170$ K, heating rate 2.5 K/s.

come even clearer in the next section. The surface composition above 350 K is quite similar for spectra 3d-3k, regardless of the initial hydrazine exposure, and α_1 saturates in fig. 3d.

From pure NH₃/Ru(001) layers, ammonia desorption is observed up to about 330 K [29] as in the hydrazine layers which are studied here. Indeed, the NH₃ peak at 280 K in fig. 4 is very similar to α_1 -NH₃ in ref. [29]; therefore we suppose the presence of adsorbed ammonia here also. This must be a decomposition/reaction product of N₂H₄. However, no feature analogous to our NH₃ peak at 225 K is found in the pure NH₃/Ru(001) system. This peak appears at the same coverage as α_2 hydrogen and is probably caused by some reaction, because at the same temperature strong desorption of N₂ is also observed (fig. 5).

The N_2 TPD spectra exhibit peaks at 225, 280 and 780-670 K. The peaks at 225 and 280 K are in coin-



Fig. 5. TPD spectra for m/e=28 (N₂) from N₂H₄/Ru(001) at increasing hydrazine doses. Atomic nitrogen coverage for T>500 K (in ML): (a) 0.09, (b) 0.16, (c) 0.20, (d) 0.25, (e) 0.29, (f) 0.32, (g) 0.33, (h) 0.34, (i) 0.35, (j) 0.36. $T_{ad}=170$ K, heating rate 2.5 K/s.

cidence with NH₃ peaks and are probably the result of a concerted N₂H₄ decomposition/NH₃ rearrangement reaction. Molecular nitrogen must be formed simultaneously with NH₃ and atomic hydrogen. While NH₃ and N₂ must desorb immediately (molecular N₂ is stable on Ru(001) only to at most 130 K), H_{ad} must stay on the surface (see also the H₂ TPD spectra in fig. 3). Therefore, the existence of intact hydrazine above 280 K can certainly be excluded. Between 220 and 270 K the adsorbate layer is probably a composition of various species, with H, N₂H_x (x=1,...,3) and maybe also NH₃ and N₂H₄.

For T above 450 K, only atomic nitrogen remains on the surface, which desorbs recombinatively between 570 and 1000 K. Regular second order desorption is observed for small N coverage (fig. 5a and 5b) with symmetric peaks which shift to lower T with increasing coverage. At higher coverage, additional TPD features are formed at the low temperature side. An estimation of the desorption energy according to Chan et al. [28] gives 112 kJ/mol, whereas the method of Tronconi and Lietti [30] yields 120 kJ/ mol.

No extra LEED pattern is observed after adsorption of hydrazine at 170 K. Only after heating of the saturated layer to 300 K a (2×2) pattern is formed which reaches its maximum brilliance at 350 K. This pattern is observable up to approx. 400 K and vanishes rapidly at higher T. At approx. 450 K, i.e. above the last H_2 peak, the new structure in fig. 6 appears. It can be described as a split $(\sqrt{3} \times \sqrt{3})$ R30° with the tips of the triangles pointing between the substrate spots; or as a strongly split (2×2) structure. The position of the spots is not constant. Rather, they move toward the $\sqrt{3}$ positions with decreasing coverage. Heating to 570 K to desorb part of the nitrogen leads to a sharp (non-split) $(\sqrt{3} \times \sqrt{3}) R 30^{\circ}$ pattern. Upon further heating these spots disappear and a diffuse background remains. We shall discuss the LEED patterns of the N/Ru(001) layer in section 3.3.5 below.

The determination of the coverage fractions for N_{ad} , $N_{2,des}$, $NH_{3,des}$ and $H_{2,des}$ is possible in an indirect way. The $\sqrt{3}$ N layer, which is prepared with optimum spot intensity by heating the hydrazine layer to 570 K, should correspond to an N coverage of 0.33 ML, as for the $\sqrt{3}$ CO layer [31]. Indeed, taking into account the slightly different ionisation factors for the two gases, one gets $\Theta(N) = 0.33$ ML for the $\sqrt{3}$ N layer from a comparison of the respective TPD integrals. The calculated fractions of N which desorb (as N_2) above 500 K are indicated in the caption of fig. 5. The total amount of N_2 which desorbs from a layer initially saturated with hydrazine (fig. 5) then corresponds to $\Theta_N = 0.45$ ML.

The amount of recombinatively desorbing H₂ (fig 3; $\alpha_1 + \alpha_2$) can be determined independently by comparison with hydrogen monolayer desorption [18]; the result is $\Theta_{H(max)} = 0.6$ ML. At N₂H₄ saturation, the two peaks correspond to roughly equal amounts (α_1 : 0.32 ML, α_2 : 0.28 ML).

From these values, the fraction of NH_3 can be determined. The total N and H amounts must have a ratio of 1:2 (N_2H_4), as during adsorption at 170 K no disproportionation with simultaneous desorption of reaction products (which can be expected at higher adsorption temperatures) was observed. At given





Fig. 6. LEED pattern observed after heating a saturated hydrazine layer to 570 K (a) and schematic drawing (b).

partial N and H coverages of 0.45 and 0.6 ML, respectively, the ratio of 1:2 can only be obtained if the desorbing ammonia fraction corresponds to 0.3 ML. From this, an initial total N coverage of 0.75 ML and of $\Theta_{\rm H}$ =1.5 ML is calculated. Therefore, the hydrazine saturation coverage is 0.37 ML, if dissociation upon adsorption is neglected for the moment (we will address this question below). These values have of course to be taken as estimates.

A strong decrease of the work function upon adsorption of hydrazine can be expected because of the high electrostatic dipole moment (gas phase 1.9 D) and electron donor character [27] of N₂H₄ (this is similar to ammonia). For the saturated chemisorbed layer, the work function decreases by 2.9 eV. The change in $\Delta \Phi$ upon additional adsorption of multilayers is less than 50 meV. Fig. 7 shows the change of the work function (hydrazine multilayers) as a function of increasing surface temperature. The removal of the multilayer at ≈ 170 K is virtually undetectable on this scale. The steep increase of Φ at ≈ 210 K starts only after the complete removal of the multilayers (compare fig. 1). This is coincident with the first appearance of desorbing NH_3 and N_2 , corroborating its connection with a surface reaction in this temperature range. A plateau with $\Delta \Phi \approx -0.7$ eV relative to bare Ru(001) is found at 320-400 K before $\Delta \Phi$ increases again. The (2×2) -LEED structure (see above) is observable in the temperature range of this $\Delta \Phi$ plateau. The adsorbate layer should be well-defined between 320 and 400 K (see the following section). Certainly, there must be a NH_x -species on the surface in this range, as indicated by the α_1 -H₂ peak at higher temperature. As explained earlier, this peak is likely to be reaction limited by the scission of N-H bonds.

The rupture of these N-H bonds and the related desorption of α_1 -H₂ goes along with a further increase of Φ by 1.05 eV. With recombinative desorption of N₂ up to 1000 K, Φ comes back to the original



Fig. 7. Change in the work function of hydrazine/Ru(001) as a function of crystal temperature. Initial layer: multilayers, prepared at 150 K. Up to 180 K $\Delta \Phi$ stays constant within 30 meV.

value of the clean surface. From this, the average dipole moment per N_{ad} atom can be estimated. With $\Theta_N = 0.37$ ML and $\Delta \Phi = +0.35$ eV we get a dipole moment of 1.06×10^{-30} Asm (0.32 D) per N_{ad} which is similar to that for O/Ru(001) at low coverage (0.29 D) [32].

3.3. Thermal evolution of the chemisorbed layer

The thermal evolution of hydrazine/Ru(001), as tested by vibrational spectra, was investigated especially in view of possible intermediate species which may form during the decomposition. The desorption products H_2 , N_2 and NH_3 and the lack of molecularly desorbing hydrazine strongly suggest such reactions. Therefore one can expect to identify reaction and dissociation intermediates via vibrational spectroscopy. The figs. 8 and 9 show HREEL spectra of the thermal evolution of saturated N_2H_4 and N_2D_4 layers prepared by desorption of multilayers. The spectra can be classified essentially into four temperature regions:

- region (i): T < 220 K, region (ii): $220 \text{ K} \le T < 300$ K, region (iii): $300 \text{ K} \le T < 430$ K,
- (11): 500 R < 1 < 450
- region (iv): T > 430 K.

These regions correspond to consecutive phases of hydrazine decomposition. In the following it will become obvious that characteristic surface species can be identified in each temperature region.

3.3.1. Region (i) (T < 220 K)

In this region, first the spectra characteristic for hydrazine multilayers are observed, as discussed in section 3.1. Heating to 180 K leads to nearly complete desorption of the multilayers. The 1100 cm⁻¹ peak is reduced by a factor of four with respect to the elastic peak compared to the multilayer spectrum, whereas the loss peaks at 880, 1330 and 1600 cm⁻¹ essentially stay at constant intensities. The ν_4 mode (1330 cm⁻¹) can be identified more clearly because ν_{11} (1230 cm⁻¹) has disappeared. On the other hand, a slight intensity increase is observed in the N-H stretch region.

Probably there are contributions of residual multilayers and the chemisorption layer in the spectra at 180 K. Especially the strong reduction of the 1100 cm^{-1} peak is remarkable. In section 3.1 the main



Fig. 8. Vibrational spectra (specular direction) of a saturated chemisorbed N_2H_4 layer heated to the indicated temperatures, measured at 120 K. Dots: data points; solid line: Fourier smooth.

contribution to this peak was attributed to ν_{12} (a-HNH wag) because of its high intensity. The modified intensity suggests relatively strong structural differences between the first layer and the multilayers which probably are mainly due to a definite orientation in the monolayer.

Above the multilayer desorption no molecular hy-

drazine is found in TPD. Therefore we have to clarify the question if hydrazine does form a molecularly chemisorbed monolayer on the surface, and if such a layer can be prepared by desorption from multilayers, respectively. To this end, spectra obtained after low hydrazine dose (≈ 0.3 L at 150 K) are useful. However, because we had to dose hydrazine through



a tube (see above), higher doses led to rather inhomogeneous layers, as indicated by multilayer features in the spectra. Therefore we present only the low coverage layer and do not attempt a systematic increase of the coverage.

A comparison of figs. 10 (low coverage; 170 K) and 8 (saturated chemisorbed layer; 180 K) shows the same structures (albeit with minor frequency shifts and lower intensity in fig. 10) in both spectra. Therefore there should be chemically identical or at least very similar species in both cases.

Ammonia can be safely excluded as dominant species in fig. 10 (170 K). This is clear from a comparison of our TPD and HREELS spectra with the TPD work on $NH_3/Ru(001)$ of Benndorf and Madey [29] as well as the HREELS spectra of Parmeter et al. [33]



Fig. 9. Vibrational spectra (specular direction) of a saturated chemisorbed N_2D_4 layer heated to the indicated temperatures, measured at 120 K. Dots: data points; solid line: Fourier smooth.

for this system. At low coverage, ammonia exhibits a single HREELS loss (δ_s at 1120 cm⁻¹). In fig. 10 (170 K) there is a loss at 1110 cm⁻¹, but the other modes at 395, 1630 and 3305 cm⁻¹ clearly lead to the conclusion that ammonia is at most a minority species in

this layer. Rather, the spectrum of fig. 10 (170 K) is consistent with molecular hydrazine which we show next.

In principle, there is the possibility of end-on or side-on adsorption. In the first alternative, the mole-



Fig. 10. HREEL spectra of N_2H_4 at low coverage (≈ 0.3 L at 150 K) and their thermal evolution. Dots: data points; solid line: Fourier smooth.

cule would be bonded mainly via the free electron pair of one amino group. Consequently, the N–N axis would not be oriented parallel to the surface. The symmetry of such a configuration would be C_1 . All modes are dipole allowed in this configuration and a vibrational spectrum similar to that of the multilayer is expected. This disagrees with experiment, especially concerning the relative intensities of the modes (cf. figs. 8 and 10 with fig. 2). Therefore, such an end-on configuration can be excluded, in agreement with the conclusions of Truong et al. [7]. These authors discarded an end-on configuration on the basis of their XPS data.

In the gas phase at room temperature, N₂H₄ adopts

exclusively the gauche configuration. The resulting C₂ symmetry is then preserved if the molecule adsorbs with the N–N axis parallel to the surface. The dipole allowed modes in this case are ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , ν_6 , and ν_7 . The mode assignment in this case is ν_1 , $\nu_2 \approx 3310$ cm⁻¹, $\nu_3 = 1630$ cm⁻¹, $\nu_5 = 1110$ cm⁻¹ and $\nu_7 = 395$ cm⁻¹. The dynamic dipole moments of ν_4 and ν_6 are probably too small to make these modes observable after a small dose (0.3 L).

However, the energy barrier between the gauche and the cis configuration is only $\approx 42 \text{ kJ/mol}$ [34]. This barrier may be overcome by the energy gain upon adsorption by the formation of Ru-N bonds. Adsorption in cis configuration with the N-N axis parallel to the surface would lead to C_{2v} symmetry. In this case ν_1 , ν_3 , ν_5 and ν_6 belong to the A₁ representation and are dipole allowed, whereas all other modes are forbidden in dipole scattering (see also table 2).

The mode assignment for fig. 10 (170 K) would then be as follows: ν_1 (s/s HNH stretch): 3310 cm⁻¹, ν_3 (s-HNH scissor): 1630 cm⁻¹, ν_5 ("N–N" stretch): 1110 cm⁻¹. The missing ν_6 (s-HNH wag) could be made plausible because of its small dynamical dipole moment. The strong 395 cm⁻¹ loss would then have to be assigned to ν_T (Ru–N₂H₄) in this case which, however, appears too high in frequency.

On the other hand, comparison with the gas phase spectra [23] suggests that the 395 cm⁻¹ loss is due to ν_7 (NH₂ torsion) because of its relatively high intensity. A loss at 285 cm⁻¹ is also found in the N₂D₄ spectra for low coverage (not shown). The frequency ratio of 1.34 supports this interpretation, so that C₂ symmetry (gauche configuration) is more probable. However, in either configuration (C₂ or C_{2v}) this mode indicates molecular adsorption, because for a Ru-NH₂ complex, for example, one would expect completely different frequencies (see below). Furthermore, the 3305 cm⁻¹ peak is relatively broad, which suggests that it is composed of two or more modes (ν_1 and ν_2 are dipole allowed for C₂ symmetry).

In summary, we can conclude that hydrazine adsorbs molecularly on Ru(001), at least at 170 K and low coverage. The N-N axis is oriented parallel to the surface. Although the results favor the gauche configuration, a definitive decision between gauche (C_2) and cis $(C_{2\nu})$ configuration of the adsorbate cannot be drawn.

3.3.2. Region (ii) (220 KT \leq T \leq 300 K)

In this temperature region, the spectra show major modifications (fig. 8). The specular intensity of the N-H (N-D) stretch vibrations has decreased considerably. At 250 K, the N-H intensity increases again. In parallel, we observe a shift from 3330 cm^{-1} (220 K) to 3380 cm⁻¹ (300 K). A double peak develops in the range $1500-1700 \text{ cm}^{-1}$. The low-energy peak (1550–1570 cm^{-1}) gains maximum intensity between 234 and 253 K to disappear completely up to 300 K. In parallel, the 880 cm⁻¹ peak gains considerable intensity up to 220 K to dominate the spectrum between 230 and 270 K. This peak disappears at 300 K. We will discuss below whether this mode is indicative of a new species. Its frequency stays constant within 5 cm^{-1} . Therefore the responsible species should not be subject to major structural changes in this temperature region.

The multilavers were dominated by one vibrational peak in the region 1000-1200 cm⁻¹ whose major contribution has been attributed to the v_{12} mode. This is also the case for the monolayer. Starting at 220 K, its intensity decreases continuously with increasing temperature. In parallel, a shoulder at the high frequency side develops into a new peak at 1150 cm⁻¹ (273 K). At 300 K, this mode shifts to 1170 cm⁻¹ and dominates the spectrum, before it disappears at higher temperature. A further new peak is observable for T > 220 K at 475 cm⁻¹. This peak shifts up to 570 cm⁻¹ at 273 K and further at even higher temperature (see temperature regions (iii) and (iv) below). A frequency of 475 cm⁻¹ seems to be too low for a genuine Ru-N stretch mode (this mode is at $\approx 600 \text{ cm}^{-1}$; see region (iv)); therefore we interpret this peak as a $\nu(Ru-NH_x)$ mode. Indeed, the shift to

Table 2

Comparison of the fundamental modes of hydrazine and their symmetry under the assumption of C_2 -, C_1 - or C_2 v symmetry of hydrazine on the surface (see text). "+"=allowed in dipole scattering, "-"= forbidden in dipole scattering. See also table 1 for abbreviations

	ν_1	ν_2	V ₃	ν_4	ν ₅	ν_6	ν_7	ν_8	vg	ν_{10}	ν_{11}	v_{12}
mode	str	str	scis	twi	N-N	wag	tors	str	str	scis	twi	wag
C ₂	Α	Α	Α	Α	Α	Α	Α	В	В	В	В	В
	+	+	+	+	+	+	+	-	_	_		_
C,	Α	Α	А	Α	Α	Α	Α	Α	Α	Α	Α	Α
	+	+	+	+	+	+	+	+	+	+	+	+
C _{2v}	A ₁	B ₂	A ₁	B ₂	A_1	A_1	A ₂	B ₂	A ₂	\mathbf{B}_1	A ₂	\mathbf{B}_1
	+	-	+	-	+	+	-	_	_	_	-	_

500-600 K coincides with the removal of H (fig. 3).

The loss at 1670–1690 cm⁻¹ (220–273 K) is due to slight CO contamination. This can be proven by additional adsorption of CO at 270 K (not shown). Such low C-O stretch frequencies on Ru(001) are usually only observed in coadsorption of highly electropositive adsorbates such as toluene [19] (1600- 1620 cm^{-1}), ammonia ($1650-1720 \text{ cm}^{-1}$) [35,36] or alkalis (1350-1625 cm⁻¹) [37,38]. Up to 280 K the work function is at -1.5 eV with respect to the clean surface. This is similar to the value for saturation with toluene (-1.6 eV [19]). In both systems the low-frequency CO state is observed. Probably the local electric field, connected with a site shift [39] is therefore responsible for the formation of this CO species because of the very different chemical environments (this system, toluene, NH₃, alkalis) in which this species is observed.

The TPD spectra of figs. 5 and 4 show massive desorption of N_2 and NH_3 in the region 220–280 K. Simultaneously, the vibrational spectra exhibit drastic changes, as described. Therefore, we can proceed from the assumption that reactions start in this range which change the adsorbate layer fundamentally.

Let us consider the 1570 cm^{-1} mode first (fig. 8, 220 K). In section 3.1, this mode was attributed to the NH₂ deformation mode (HNH scissor; δ_{NH_2}). Its presence is clear evidence of intact NH₂ groups up to 280 K. Now we address the question if these NH_2 groups are part of larger entities or if they are bound directly to the surface. In the latter case, one would have Ru-NH₂. In all known X-NH₂ compounds, the NH_2 group together with the substituent (X) adopt a pyramidal structure because of the presence of the free electron pair [27,40]. For NH₂/Ru(001), this leads to Cs symmetry. A schematic drawing of NH₂/ Ru(001) in C_s configuration is shown in fig. 11, together with its fundamental modes. In this configuration, δ (HNH scissor), ν_s , T_{ν} , T_z (hindered translations) and R_x (hindered rotation) are dipole allowed (see table 3).

The new (or at least considerably enhanced) modes at 495 and 880 cm⁻¹ can then be attributed to T_z and R_x , respectively. The continuous shift of T_z from 495 cm⁻¹ at 220 K to 570 cm⁻¹ at 273 K (and further to 600 cm⁻¹ at 480 K) must be connected with the successive split-off of hydrogen, which eventually leads to atomic N_{ad}. The corresponding assignment for the



Fig. 11. Schematic representation of the structure and fundamental modes of $NH_{2,ad}$ for C_s symmetry with σ_{yz} as mirror plane. See also table 3.

deuterated species (ND₂/Ru(001)) is then (for T=234 K; not shown in fig. 9): $\nu_{s/a}$ (ND₂): 2450 cm⁻¹, δ_{sc} (ND₂): 1140 cm⁻¹, T_z 490 cm⁻¹ and R_x 760 cm⁻¹ (see table 4).

The loss at 1030–1040 cm⁻¹ (220–253 K) cannot be attributed to any NH₂/Ru(001) mode. But in view of the complex TPD spectra, which indicate (maybe coupled) chemical reactions, one cannot expect that the adsorbate layer consists of a single adsorbate species in the temperature region 220–270 K. The H₂ desorption between 300 and 330 K (α_2 peak, fig. 3) and the desorption of ammonia at 220 and 280 K (fig. 4) strongly suggest the presence of N₂H_x (x=1, ..., 3) and/or NH₃ in addition to the NH₂ species characterized above.

The loss at 1150 cm^{-1} which evolves from the edge of the 1030 cm⁻¹ peak between 234 and 273 K is indeed characteristic for δ_s (inversion mode) of ammonia at low coverage [33]. This mode is at 900– 910 cm⁻¹ for ND₃ and can clearly be seen in fig. 9 between 253 and 300 K. This mode disappears after the completion of the second NH₃ TPD peak (fig. 4). As mentioned above, the second NH₃ peak is characteristic for desorption of *adsorbed* ammonia. Therefore we propose that part of the ammonia which is formed during a surface reaction remains on the surface. Another part (maybe from another reaction) desorbs at 225 K. Then the 1030 cm⁻¹ loss peak

Table 3	
Dipole allowed $(+)$ and forbidden $(-)$ modes of $NH_{2,sd}$ for adsorption in C_s configuration. T_i : hindered translations, R_i : hir	idered
rotations; mirror plane σ_{yz} . See also fig. 11	

mode	T _x	T,	T_z	R _x	R _y	R_z	δ	ν_{s}	ν_{as}
C _s	-	+	+	+	-	-	+	+	-

indicates a N_2H_x intermediate species which is additionally formed in the course of successive dissociation and reaction of hydrazine. Possible reaction mechanisms will be considered in the discussion.

The off-specular HREEL spectrum corresponding to fig. 8 at 234 K (not shown) gives evidence that all these modes have dipole characteristics, with the exception of the ν (N-H) region (> 3200 cm⁻¹), where also major impact contributions are observed. These modes should be attributable to the asymmetric ν (NH₂) stretch vibrations. Additionally, there should be contributions of the asymmetric N-H stretch vibrations of ammonia and also of the N₂H_x intermediate species.

3.3.3. Region (iii) (300 K $\leq T \leq 430$ K)

The vibrational spectra simplify considerably for T > 300 K (figs. 8 and 9). The sudden disappearance of the R_x mode for T > 280 K indicates further fundamental changes in the adsorbate layer. For T > 300K the ammonia vibration δ_{s} loses intensity in accordance with the ammonia TPD. Only a residual loss peak is observable there for T > 350 K, which is most probably due to readsorption from the gas phase. The decrease in the δ_{sc} -NH₂ intensity (1560–1590 cm⁻¹) is completely parallel to that of the 880 cm^{-1} peak, which, according to our interpretation, is NH_2-R_x (this corroborates this assignment). In parallel, the Ru-NH_x stretch vibration shifts continuously to 570 cm⁻¹. This tendency is observable even from 270 K on. With rising temperature and further split-off of hydrogen, this mode can of course not be attributed to a genuine Ru-NH₂ stretch mode.

For T > 270 K, two other modes gain intensity. In the N-H stretch region, a loss at 3350 cm⁻¹ appears, which reaches its maximum intensity at 360-390 K. Its half-width is only 70 cm⁻¹ at 360 K which is considerably sharper than in the temperature region (ii) and in the multilayers. Its frequency is shifted to higher values by 40 cm⁻¹. This small half width is indicative for a single mode (in contrast to the spectra at lower temperature).

The other mode which gains intensity for T > 270 K (although to a smaller extent) is at 1350–1360 cm⁻¹. These modes can be attributed to the same adsorbate species. Taking into account the successive loss of hydrogen, we conclude that this species is NH/ Ru(001).

In the H₂ TPD spectrum, the temperature region (iii) falls between the two H₂ peaks (fig. 3k), before the broad N₂ structure and after the final desorption of ammonia. The work function exhibits a plateau between 300 and 400 K, compared to the relatively strong variation before and after this region. As mentioned above, in this region the first LEED superstructure can be found: a (2×2) pattern.

Therefore, the adsorbate layer should be chemically relatively stable and of relatively well defined structure. Even though the N and H coverages of 0.36 ML and 0.32 ML, respectively, cannot be brought into good accordance with a homogeneous (2×2) or (2×1) structure, the (2×2) LEED structure is unequivocally connected with the NH groups: both features disappear for T > 400 K, together with simultaneous desorption of hydrogen (thermal disorder might also contribute to the disappearance of the LEED structure).

The modes for the NH/Ru(001) complex are then assigned as follows: ν (Ru-NH) 570 cm⁻¹, ν (N-H) 3370 cm⁻¹ and δ (Ru-N-H) 1350-1360 cm⁻¹. For the deuterated species ND/Ru(001), the assignment is ν (Ru-ND) \approx 570 cm⁻¹, ν (N-D) 2455 cm⁻¹ and δ (Ru-N-D) \approx 1060 cm⁻¹ (fig. 9; 360 K). All these modes show essentially dipole character. This excludes a linear Ru-N-H arrangement, because in this case (C_{6v} or C_{3v} symmetry) the δ (Ru-N-H) bending vibration would be dipole forbidden.

To determine the geometric structure of the Ru-NH complex, a comparison with imidocomplexes of transition metals is helpful [41]. The experimental data on imido complexes for the Mn and Fe triads are essentially limited to Re and Os. In these complexes, the metal-N-H angle falls within the range of 120° to 130°. This is well reproduced by ab initio calculations by Cundari [41]. The same holds for the (calculated) values of the Ru-imidocomplexes $Ru(NH)_3$, $Ru(0)_3(NH)$ and $Ru(NH)(H)_4$. Therefore, a bent configuration is favored by theoretical considerations also. Such a NH/Ru(001) (+N) layer may be a good candidate for future ESDIAD measurements. Because of the simple chemical composition of the adsorbate layer for T > 350 K, the Ru-N-H angle should be determinable in a relatively straightforward manner from angular data of H⁺ emission.

Because of the C_s symmetry of such a bent NH/ Ru(001) species the three fundamental modes are dipole allowed (see fig. 12). The CO impurities (ν_{Ru-CO} 430 cm⁻¹, $\nu_{1,C-O}$: 1700 cm⁻¹, $\nu_{2,C-O}$: 2000 cm⁻¹) transform into a single state between 300 and 360 K to disappear completely by 450 K.

3.3.4. Region (iv) (T > 430 K)

Above the last H_2 peak only desorption of N_2 is observed. This H_2 peak must result from immediate recombinative desorption of the H atoms stemming from scission of the N-H bond, as seen from its correlation with the disappearance of the N-H vibration, and its high temperature compared to normal H_2 desorption.

Readsorption of hydrogen on the remaining N/ Ru(001) layer at 120 K did not lead to reformation of N-H bonds upon heating: the corresponding losses did not reappear in HREELS. The readsorbed hydrogen desorbed like α_2 hydrogen, with similar peak shape and temperature as discussed before, corroborating its assignment to recombinative desorption of normal adsorbed H atoms.

The vibrational spectrum exhibits only one loss for T > 450 K. It is shifted up by 30 cm⁻¹ to 600 cm⁻¹



Fig. 12. Configuration of NH/Ru(001).

after dissociation of the last N-H bonds. This loss can be attributed to the Ru-N stretch vibration of atomic nitrogen. A comparison with similar adsorbates (O/ Ru(001) [42], S/Ru(001) [43]) supports a threefold hollow site as the most probable adsorption site.

Nitrogen desorbs recombinatively for T > 530 K. For small nitrogen coverage, an estimation of the desorption energy according to Chan et al. [28] yields 120 kJ/mol under the assumption of second order desorption. With the dissociation energy of N₂ in the gas phase (945.3 kJ/mol (298 K) [44]) we get an estimate of 533 kJ/mol for the N_{ad} surface bond. For higher coverage, the peak shape deviates considerably from second order desorption which indicates lateral interactions in the nitrogen layer.

3.3.5. LEED pattern of the N/Ru(001) layer

An interesting feature of the pure nitrogen layer is the LEED pattern which can be described as $(\sqrt{3} \times \sqrt{3})$ R30° with split spots (fig. 6). As mentioned above, the $\sqrt{3}$ spots are replaced by equilateral triangles with one spot at every tip. The tips of the triangles point exactly between the substrate spots. An equivalent description for this pattern is a split (2×2) structure. In this case, the (2×2) spots are replaced by double spots.

The split is coverage dependent. An increase of the temperature and desorption of part of the nitrogen leads to a smaller split. Eventually, an unsplit, sharp $(\sqrt{3} \times \sqrt{3})$ R30° pattern can be observed. However, we did not succeed in preparing an unsplit (2×2) structure, not even with repeated dosing-dissociation cycles of hydrazine.

This split of the superstructure spots can be accounted for by two mechanisms: the first is the formation of a rotated, homogeneously compressed phase for $\Theta_N > 0.33$ ML. In this case, the layer would be made up by two different rotated domains with hexagonal unit mesh [45]. The second possibility is the formation of domain walls [46].

The first mechanism is characteristic for physisorbed adsorbates and can be found in the systems Ne/Ru(001), Ar/Ru(001) and Xe/Ru(001) [47]. There the strength of the adsorbate-adsorbate interaction is comparable with the strength of the adsorbate-substrate interaction. Structures with fixed spots are formed by this mechanism. The transition from one pattern to the next is discontinuous, i.e. the spots which are caused by one structure disappear while the next ones appear. But for chemisorbate species (e.g. for S/Ru(001) [43]) the adsorbate-substrate interaction dominates clearly.

A more satisfactory explanation for the structure observed in the present case of N/Ru(001) and for its thermal as well as coverage dependency can be given in terms of the second mechanism, i.e. the formation of domain walls. For the TPD-derived coverage of $\Theta_N = = 0.36 - 0.37$ ML, the domain walls can be heavy or superheavy, with striped or hexagonal symmetry. Zeppenfeld et al. [46] gave a method to determine the type and symmetry of domain walls from the number and orientation of the superstructure spots, based on kinematic calculations. With this, our N/Ru(001) pattern can be explained as being caused by superheavy walls with hexagonal symmetry.

The relation between the mean distance of the walls l and the coverage Θ is given by [48]

$$\boldsymbol{\Theta} = \frac{1}{3} \left(1 + 2 \, \frac{a}{l} \right),$$

where a is the length of a substrate lattice vector. In reciprocal space this relation translates to

$$\boldsymbol{\Theta} = \frac{1}{3} \left(1 + \sqrt{3} \, \frac{\boldsymbol{\epsilon}}{a^*} \right),$$

with the corresponding values of $\epsilon = 4\pi/3l$ [46] and a^* . For illustration, ϵ is the distance between the center of gravity of the triangles spanned by the split spots and the spots themselves in fig. 6. With $\Theta_N = 0.36$ -0.37 ML, as determined with TPD, one gets l/a=25-18.1. The LEED photo gives a ϵ/a^* ratio of 0.09 which yields a coverage of $\Theta_N = 0.387$. The difference of the two values for $\Theta_N(<5\%)$ can be well accounted for by the uncertainty in measuring the exact position of the LEED spots. Fig. 13 shows a model for superheavy domain walls with hexagonal symmetry under the assumption that all N_{ad} atoms occupy the same type of threefold hollow adsorption sites. Since a decision between fcc and hcp type hollow sites is not possible with our methods, other models could be derived in which both site types would be occupied.

Fig. 13. Local structure for superheavy domain walls in the system N/Ru(001) under the assumption that all N_{ad} atoms occupy the same type of hollow adsorption sites. Large circles: Ru atoms; small circles: N atoms. Domain walls are indicated as lines.

4. Discussion

We briefly recapitulate the main results for the thermal evolution of hydrazine on Ru(001):

-At 170 K, hydrazine adsorbs predominantly in molecular form; the corresponding work function change is -2.85 eV. Slight dissociation cannot be ruled out completely. For T > 220 K, the adsorbate layer changes definitely.

-No molecular desorption of N₂H₄ is observed upon heating.

-In the region 220-280 K, amino groups (-NH₂) are most probably bonded directly to the surface.

-Up to 270 K, larger dissociation products of the form N_2H_x exist, which cannot be specified more exactly, in addition to the amino groups.

-Ammonia as dissociation and/or reaction prod-

uct can be identified on the surface between 230 and 300 K.

-Imide groups (-NH) can be identified for T > 280K. Between 360 and 400 K, they represent the only species on the surface containing N-H bonds.

-Two H₂ TPD peaks of different nature are observed. The first (α_1) appears between 390 and 450 K and is limited by the scission of N-H bonds, while the second (α_2) between 280 and 340 K is caused by recombinative desorption of H/Ru(001).

-Atomic nitrogen is the only residual adsorbate for T > 480 K up to its recombinative desorption above 650 K.

4.1. Reaction paths

Hydrazine turned out to be very reactive on Ru(001). N₂, NH₃ and H₂ are found as desorption products. Gross equations for these products can be listed together with an estimation of the total reaction enthalpies [49]:

$$N_2H_4(g) \rightarrow \text{adsorbates} \rightarrow N_2(g) + 2H_2(g) ,$$

$$\Delta H = -93.2 \text{ kJ/mol} , \qquad (1)$$

 $3N_2H_4(g) \rightarrow adsorbates \rightarrow 4NH_3(g) + N_2(g)$,

$$\Delta H = -187.7 \text{ kJ/mol}. \qquad (2)$$

A further, highly exothermic gas phase reaction of hydrazine with one of its dissociation products is

$$N_2 H_4(g) + H_2(g) → 2NH_3(g)$$
,
 $\Delta H = -183.9 \text{ kJ/mol}$. (3)

On the surface, this reaction is conceivable in the following way:

$$N_2H_4(a) + H(a) \rightarrow N_2H_5(a)$$
,
 $N_2H_5(a) + H(a) \rightarrow 2NH_3(g)$. (4)

Such a mechanism was proposed by Ertl and Tornau for the catalytic decomposition of hydrazine on polycrystalline Pd [50]. However, this preassumes the coexistence of molecular hydrazine with some of its decomposition products. On the surface it is conceivable as two-step process or in the form of a concerted reaction.

A second possibility to get to NH₃ is

$$N_2H_4(a) \to 2NH_2(a)$$
, (5)

$$NH_2(a) + H(a) \rightarrow NH_3(g) . \tag{6}$$

This would work under the condition of coexistence of $NH_2(a)$ and H(a). In this case, there have to be at least two parallel reaction paths. Reaction 6 has been considered as the last step in the catalytic production of ammonia over iron catalysts (Haber-Bosch method) [51-53].

In section 3.3.1 we showed that at 170 K most of the hydrazine is adsorbed molecularly. This leads to the question if the primary dissociation step is the scission of the N–N or of the N–H bonds, or a combination of the two. The following primary and possibly concurring dissociation steps with molecular hydrazine as starting point are conceivable:

$$N_2H_4(a) \to 2NH_2(a)$$
, (7)

$$N_2H_4(a) \rightarrow 2H(a) + N_2H_2(a)$$
, (8)

$$N_2H_4(a) \to H(a) + N_2H_3(a)$$
. (9)

In case of partial dissociative adsorption, these processes may take place immediately upon adsorption.

The TPD spectrum exhibits N_2 and NH_3 peaks at 220 K; the work function change suggests that the preceding reactions (7)–(9) take place in the same T range indicating parallel or nearly parallel scission of the N–N and N–H bonds. Furthermore, $NH_2/$ Ru(001) can be identified on the surface for T > 220 K. Therefore, a gross reaction equation may have the following form (without taking into account dissociative adsorption):

$$N_{2}H_{4}(a) \xrightarrow{220 \text{ K}} NH_{3}(g) + N_{2}(g) + NH_{2}(a)$$
$$+ N_{2}H_{x}(a) [+H(a)], \qquad (10)$$

with unknown stoichiometry. This accounts for N_2H_x species, which should be present in addition to the amino group. The exact point of hydrogen split-off

(and adsorption on the surface) cannot be determined at this moment.

The next step has to yield primarily N_2 from some dissociation reaction, because molecularly adsorbed N_2 desorbs at much lower temperature from Ru(001). In addition, a small amount of NH₃ should be formed:

$$N_2H_x(a) \xrightarrow{up \text{ to } 280 \text{ K}} N_2(g) + NH_3(a) [+H(a)].$$
(11)

The appearance of the δ_s -NH₃ mode and in parallel the disappearance of the N–N mode (1030 cm⁻¹, see fig. 8) can be explained by this reaction step. The evolving ammonia then desorbs at ≈ 280 K (fig. 4). Nearly parallel to this, the amino groups should dissociate by 300 K (eq. (12)). This appears to happen by split-off of one hydrogen atom, leading to surface imide groups (NH/Ru(001)). Hydrogen then desorbs recombinatively to form the α_2 peak. Additionally, there might be contributions of H(a) from an earlier reaction step (eqs. (9), (10)) which now desorbs:

$$NH_{3}(a) \xrightarrow{280 \text{ K}} NH_{3}(g) ,$$

$$NH_{2}(a) \xrightarrow{280-300 \text{ K}} NH(a) + H(a) ,$$

$$H(a) + H(a) \xrightarrow{300-330 \text{ K}} \alpha_{2} - H_{2}(g) . \qquad (12)$$

As a competing process to eqs. (12) the following reaction is also conceivable:

$$NH_2(a) + H(a) \rightarrow NH_3(a) \rightarrow NH_3(g) . \tag{13}$$

For T > 350 K, NH/Ru(001) is the major adsorbate species. This indicates that the scission of the N-N bonds is completed at lower T than the rupture of the N-H bonds. In section 3.2 the coverages of N (for T > 330K) and hydrogen (α_1) were estimated as 0.36-0.37 ML (N) and 0.28 ML (H), for initial saturation of hydrazine. From this discrepancy it can be seen that the adsorbate layer even for T > 350 K is no pure NH/Ru(001) layer. Rather, even before the scission of the imide N-H bonds a small amount of atomic nitrogen should exist in the layer. It was not possible to identify the reaction step(s), which produce these N atoms.

Certainly, the last dissociation step of hydrazine on Ru is

$$2NH(a) \xrightarrow{400-450 \text{ K}} 2N(a) + H_2\uparrow(g)$$
. (14)

This is evidenced unequivocally by the HREELS and TPD spectra. For T > 330 K, only NH and N are present on the surface, with N still a minority species. Atomic H_{ad} would desorb at T < 430 K [18]. This implies that the last and only adsorbate species after the decomposition of the imide is atomic nitrogen which desorbs recombinatively for T > 500 K according to

$$N(a) + N(a) \xrightarrow{>500 \text{ K}} N_2(g) . \tag{15}$$

From all this it can be seen that detailed statements for the fundamental decomposition processes and their stoichiometry are difficult. This holds especially for the region of the complex primary (and maybe concerted) reactions. For example, it is not clear at all how eqs. (10) and (11) have to be split into the correct individual processes.

Nevertheless, steps (12), (14) and (15) can be established with a high degree of certainty. Especially, our results contain a direct proof of reaction (14). The primary reaction steps seem to be essentially parallel scission of the N–N bond and of the N–H bonds, where the first mechanism is completed at lower temperature. The third alternative, direct hydrogenation of N₂H₄, appears to be at most a minority channel.

4.2. Comparison with other surfaces

Hydrazine turns out to be very reactive on all surfaces of metal single crystals, polycrystalline materials and semiconductors which have so far been investigated. This is desired in view of possible applications. In these, hydrazine may be used as nitrogen carrier to deposit atomic nitrogen on surfaces. N_2 is not very useful for this purpose on most metals and semiconductors because of its high dissociation energy of 945.3 kJ/mol [44].

The tendency for dissociative adsorption decreases

for transition elements from left to right in the periodic system. For example, nitrogen adsorbs dissociatively on Mo(111), W(100) and Fe [54], while the sticking coefficient for dissociative adsorption (T < 300 K) is very small on metals like Ru, Pd, Rh, Pt and Ir [54]. Iron is used as catalyst in the industrial Haber-Bosch synthesis of ammonia, where the scission of the N-N triple bond is considered as the rate limiting step [55]. This is followed by stepwise hydrogenation of the atomic nitrogen via intermediate imide and amino species to ammonia which desorbs.

We can therefore rationalize why we do not observe ammonia synthesis from N(a) and H(a) under UHV conditions. Post-adsorption of hydrogen on N/Ru(001) at 115 K and subsequent heating of the coadsorbate layer did not result in the formation of any N-H bonds (section 3.3). Hydrogen desorbs in molecular form between 300 and 350 K, exactly like hydrogen which is adsorbed in atomic form in addition to NH/Ru(001) for T < 330 K (α_2 -H₂). The activation energy for the formation of N-H bonds seems to be higher than the binding energy of hydrogen on the surface. In addition, under UHV conditions the H concentration may be too low for the formation of N-H bonds. This is a typical manifestation of the "pressure gap". To test a possible reaction of NH with H, experiments at higher pressure are desirable, for example interaction of NH with H₂ at high H₂ partial pressure followed by quenching under high H₂ pressure.

The last step which is necessary for ammonia synthesis, i.e. the reaction

$$NH_2(a) + H(a) \xrightarrow{\approx 280 \text{ K}} NH_3(g)$$
 (16)

cannot be excluded completely for N₂H₄/Ru(001). NH₃ can be identified in the vibrational spectrum for T > 240 K and NH₂ disappears for T > 280 K. Simultaneously, δ_{s,NH_3} (1170 cm⁻¹) reaches its maximum intensity, and NH₃ is a major desorption product. If reaction (16) really happens, then there has to be some excess of hydrogen, because at ≈ 300 K there is additional recombinative desorption of H₂ (α_2). NH/Ru(001), which dominates above 330 K, should then be a decomposition product of a N₂H_x species. However, there is no evidence for such a N₂H_x species above 280 K. In return, this makes the reaction 16 improbable.

The use of ammonia as nitrogen carrier is also not very efficient in most cases. Ammonia adsorbs in molecular form on Ru(001) for T < 300 K [33,29]. Simultaneously high temperature (480 K), exposure and pressure (600 s at 2.8×10^{-6} Torr) are necessary for partial dissociation and production of adsorbed N atoms [56].

Up to now, there are three published works on hydrazine on single crystal metal surfaces where vibrational spectroscopy has been employed: by Gland et al. (HREELS) on Ni(111) [1], by Alberas et al. (HREELS, TPD, XPS, UPS and TPSIMS) on Pt(111) [2] and by Truong et al. (FTIR, XPS, AES and TPD) on RU(001) [7].

The multilayer vibrational spectra of [7] are in excellent agreement with our HREEL spectra. This holds also for H₂, N₂ and NH₃ and the N₂H₄ multilayer TPD spectra. There is discrepancy in two points: Truong et al. find molecular desorption of chemisorbed hydrazine at 280 K, but do not observe any vibrational loss above 180 K attributable to an adsorbed nitrogen-hydrogen species. This is surprising, because the TPD spectra confirm chemisorbed hydrazine above 180 K, and their XPS data are compatible with the assumption of $N_m H_n$ species. These authors also come to the conclusion that chemisorbed hydrazine is oriented with the N-N bond parallel to the surface, where C_{2x} symmetry is favored according to MO calculations [7]. In this case however, at least v_5 (N–N stretch) and v_1 (s/s stretch) should be infrared active as in the multilayers. The reaction scheme suggested by Truong et al. includes $N_x H_v(ads), N_m H_n(ads)$ and $N H_x$ species. It is compatible with the decomposition processes discussed above because it contains fewer details.

Another, similar discrepancy can be found between the NH₃/Ru(001) spectra by Parmeter et al. [33] and the NH₃/Ru(001) FTIR data by Rodriguez et al. [57], which were obtained with the same methods as those of Truong et al. [7]. While the ammonia bilayer shows no absorption above 1000 cm⁻¹ in IR (contrary to mono-and multi-layers) [57], the HREELS intensities of δ_s (1145 cm⁻¹) and ν_s (3225 cm⁻¹) measured by Parmeter et al. [33] show dipole activity and dominate the vibrational spectrum above 1000 cm⁻¹.

The HREEL spectrum of a submonolayer of chemisorbed hydrazine/Ni(111) [1] is in very good agreement with our spectra at low coverage and shows the modes which are expected in "flat" adsorption geometry and C_s symmetry. Ni(111) appears to be even more reactive, and the decomposition seems to proceed via a slightly different path, because on this surface the adsorbate layer consists nearly exclusively of NH/Ni(111) for T > 285 K. The surface becomes completely dehydrogenated between 400 and 500 K leaving atomic nitrogen with ν (Ni–N) at 490 cm^{-1} ; nitrogen desorbs recombinatively between 750 and 900 K. The last dissociation step therefore is the same on Ru(001) and Ni(111). On both surfaces, N_{ad} is the most stable product in the dissociation series. Also, no molecular hydrazine is found in TPD from a chemisorption layer on Ni(111) [1].

Interestingly, a fundamentally different dissociation path has been found on Pt(111) [2]. Starting from molecularly chemisorbed hydrazine, the dissociation proceeds nearly exclusively via scission of N– H bonds. Ammonia desorption is explained by direct hydrogenation of hydrazine or one of its dissociation products. Consequently, atomic N_{ad} is missing; there is no Pt–N mode and no recombinative desorption of N₂: the N–N bond stays intact. This implies a unimolecular desorption mechanism for N₂ on Pt(111). The desorption products in this case were N₂H₄, NH₃, N₂ and H₂.

In most studies on hydrazine adsorption on metal surfaces, the last three molecules are the only species detectable in TPD, for example from Pd(poly) [50], GaAs(poly) [58], Cr(poly), Mn(poly), Fe(poly), W(poly), Re(poly), Os(poly) [59], $Si(100)(2 \times 1)$ [60], Rh(111) [4], Ir(111) [6], Ir(poly) [12], Pd(100) [3] and Rh(100) [5]. From the last two surfaces, molecular desorption of weakly chemisorbed hydrazin is also observed. An exception is Rh(poly), where also a small amount of diimine (N_2H_2) desorbs [9,10]. The proposed dissociation mechanisms are mainly based on the TPD spectra and frequently include the formation of NH₂ and NH; however in most cases without direct proof for their existence as surface species. Besides vibrational spectroscopy, more detailed conclusions can be drawn from XPS [5,8,61] and UPS [5,8] measurements. Matloob and Roberts [61] could give experimental proof for NH(ad) and $NH_2(ad)$ in the dissociation path of hydrazine on polycrystalline iron via XPS. A similar, although more detailed conclusion was drawn by Grunze [8] for Fe(111) based on UPS and XPS data.

Essentially four dissociation paths are discussed in the literature for hydrazine on metal surfaces:

(i) In the first path, the first step is the scission of the N-N bond. This leads to adsorbed amino species (reaction (5) above) which decompose typically into N and H. Recombinative desorption of N_2 and H_2 can then be found in TPD.

(ii) Reaction (5) is also the first step in the second path. NH_2 however reacts with H(ad) to ammonia (eq. (6)) which desorbs.

(iii) In the third path, the first step is the scission of N-H bonds and stepwise dehydrogenation of the fragments. In this case, N_2 is formed by a unimolecular mechanism (similar to eq. (10) or (11)).

(iv) The fourth possibility is a direct hydrogenation of hydrazine in a concerted decomposition/attachment reaction, for which one of the products is NH_3 (see eq. (4)).

The actual decomposition behavior depends strongly on the surface. For example, evidence for path (i) alone is reported for Fe(111) [8], polycrystalline iron [61] and Al foil [11], whereas path (iii) seems to be the majority channel on Pt(111) [2]. On most other surfaces the dissociation proceeds via a combination of various paths, while the exact relations cannot be quantified exactly. This holds also for $N_2H_4/Ru(001)$. Here the majority paths are most probably (i) and (iii).

The detailed desorption behavior depends on the adsorption and binding energies of all species involved as well as on the activation barriers between possible intermediates. The H₂N-NH₂ binding energy in gas phase hydrazine is 275.3 kJ/mol and the value for the H-NHNH₂ bond is 366.1 kJ/mol [44]. Therefore one might expect that the N-N bond breaks prior to the N-H bonds. However, the binding energies of the reaction products (N, H, NH, etc.) depend strongly on the substrate which may hold also for the activation energies. If, for example, the activation barrier for the reaction $N_2H_{4(ad)} \rightarrow 2NH_2$ is large compared to the one for $N_2H \rightarrow N_2H_{3(ad)} + H_{ad}$ and/or successive dehydrogenation, then a dissociation path without the scission of the N-N bond seems to be possible, as reported by Alberas et al. [2].

The desorption energy for α_2 -H₂ (with $T_p = 305$ K) was estimated as 118 kJ/mol. The corresponding value for recombinative desorption of nitrogen at low coverage was 120 kJ/mol. For Pt(111) the relevant values are 87.7 kJ/mol [62] for hydrogen and 104.5 kJ/mol [63] for nitrogen. With the gas phase dissociation energies of H_2 (436 kJ/mol [44]) and N_2 (945 kJ/mol [44]) the Ru-H (α_2) , Ru-N, Pt-H and Pt-N binding energies can be calculated. The result is Ru-H (α_2): 277 kJ/mol; Ru-N: 534 kJ/mol; Pt-H: 261.8 kJ/mol and Pt-N: 524.9 kJ/mol. Therefore, the difference between Ru(001) and Pt(111)is not very large in this respect. The different dissociation paths should therefore be caused mainly by the different activation energies for the formation of specific intermediates.

Recently, thermal nitridation of silicon with hydrazine and its methyl derivates gained interest, with emphasis on the production of thin isolating films. Such silicon nitride films exhibit an extremely high resistance against environmental influences [13]. During the thermal decomposition of N₂H₄ [13] or NH₃ [64] on Si(111)-(7×7), NH_{2(ad)} could be identified in both cases, with δ_{sc} between 1550 and 1565 cm⁻¹. NH(ad) could not be detected. Formation of NH₂ and NH could be observed by laser induced dissociation of ammonia on GaAs(100) [65]. Finally, we note that also during thermal decomposition of methyl amine (CH₃-NH₂) a short living amino group is formed [66] and stabilized by CO [67].

Tables 4 and 5 show a comparison of the NH_2 and NH modes for various surfaces and chemical environments.

5. Summary

Desorption of hydrazine multilayers proceeds in one peak; no individual layers can be resolved. At 170 K, hydrazine adsorbs mainly molecularly, although partial dissociation cannot be ruled out completely. Due to the high reactivity of hydrazine on Ru(001), no molecular hydrazine desorbs from a chemisorbed monolayer; the only desorption products from a chemisorption layer are N₂, NH₃ and H₂. The adsorption layer changes definitely for T > 220 K. Species containing an N–N bond (N₂H_x species) are detectable on the surface up to ≈ 270 K. Surface amino groups (NH₂/Ru(001) can be identified between 220

Table 4 Comparison of the NH₂ (ND₂) vibrational modes in complexes and on various surfaces. Values in cm^{-1}

NH ₂ (ND ₂)	NH ₂ ^{a)} metal complexes	NH2 *) Ni(110)(2×1)	NH2 ^{b)} Si(111)(7×7)	NH2 °) Si(111)(7×7)	NH2 ^{d)} GaAs(100)	NH2 ^{e)} Ru(001)
$\nu_{a}(NH_{2})$	3380					
		3280-3330 ^f)	3435 ^{f)}	3395 ^{f)}	3232 (2420)	3340 (2450) ^f)
$\nu_{\rm s}(\rm NH_2)$	3100, 3225					
$\delta_{\rm sc}(\rm NH_2)$	1573-1605	1520	1530 (1130)	1565	1500 (1100)	1560 (1140)
$\nu_{s}(X-NH_{2})$	500-564	505	850 (800)		850	≈ 530 (490)
$\rho_{\rm r}(\rm NH_2)$			535 (415)	887		875 (760)

^{a)} Ref. [68]. ^{b)} Ref. [64]. ^{c)} Ref. [13]. ^{d)} [65]. ^{e)} This work. ^{f)} v_s and v_a not resolved.

Table 5

Comparison of the fundamental modes for NH (ND) in complexes and on various surfaces. Values in cm⁻¹

NH (ND)	NH ^{a)} metal complexes	N₃H ^{ь)}	NH °) Si(111)- (7×7)	NH ^{d)} Ni(110)- (2×1)	NH *) Ni(111)	NH ^{f)} Ru(001)
$\nu(NH)$	2994-3400	3336	3375-3435	3240-3250	3340 (2480)	3360 (2455)
$\delta(NH)$	1410-1414	1152	1100		1270 (950)	1360 (≈1060)
$\nu(X-NH)$			≈870		620 (580)	570 (≈570)

^{a)} Ref. [41]. ^{b)} Ref. [69]. ^{c)} Ref. [64]. ^{d)} Ref. [68]. ^{e)} Ref. [1]. ^{f)} This work.

and 280 K; surface imide groups (NH/Ru(001)) are detectable for T > 280 K. Between 360 and 400 K the latter represent the only adsorption species containing N-H bonds. Additionally, ammonia is present as reaction product between 230 and 300 K. For T > 480K atomic N_{ad} is the final adsorbate in the decomposition path. Atomic nitrogen forms a domain wall structure for $\Theta_N > 0.33$ ML. Recombinative desorption of N₂ proceeds between approx. 570 and 1000 K. The bearing of these results for the mechanisms of hydrazine surface evolution have been discussed. The main results are that N-N and N-H bond scission proceed essentially in parallel, with the first being complete at lower T; quite complicated rearrangement processes result from this in the range around 220-270 K.

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References

- J.L. Gland, G.B. Fisher and G.E. Mitchell, Chem. Phys. Letters 119 (1985) 89.
- [2] D.J. Alberas, J. Kiss, Z.-M. Liu and J.M. White, Surface Sci. 278 (1992) 51.
- [3] R. Dopheide, L. Schröter and H. Zacharias, Surface Sci. 257 (1991) 86.
- [4] M.L. Wagner and L.D. Schmidt, Surface Sci. 257 (1991) 113.
- [5] W.M. Daniel and J.M. White, Surface Sci. 171 (1986) 289.
- [6] H.H. Sawin and R.P. Merrill, J. Chem. Phys. 73 (1980) 996.
- [7] C.M. Truong, J.A. Rodriguez and D.W. Goodman, J. Phys. Chem. 96 (1992) 334.
- [8] M. Grunze, Surface Sci. 81 (1979) 603.
- [9] J. Prasad and J.L. Gland, Langmuir 7 (1991) 722.
- [10] J. Prasad and J.L. Gland, Surface Sci. 258 (1991) 67.
- [11] D.W. Johnson and M.W. Roberts, J. Electron Spectry Relat. Phenom. 19 (1980) 185.
- [12] B.J. Wood and H. Wise, J. Catal. 39 (1975) 471.
- [13] Y. Bu, D.W. Shinn and M.C. Lin, Surface Sci. 276 (1992) 184.

- [14] K.L. Kostov, H. Rauscher and D. Menzel, Surface Sci. 287/ 288 (1993) 283.
- [15] K.L. Kostov, P. Jakob, H. Rauscher and D. Menzel, J. Phys. Chem. 95 (1991) 7785.
- [16] P. Feulner and D. Menzel, J. Vaccuum Sci. Technol. 17 (1980) 662.
- [17] H.A. Engelhardt, P. Feulner, H. Pfnür and D. Menzel, J. Phys. E 10 (1977) 1133.
- [18] P. Feulner and D. Menzel, Surface Sci. 154 (1985) 465.
- [19] H. Rauscher, P. Jakob, D. Menzel and D.R. Lloyd, Surface Sci. 256 (1991) 27.
- [20] F.G. Baglin, S.F. Bush and J.R. Durig, J. Chem. Phys. 47 (1967) 2104.
- [21] Y. Hamada, A.Y. Hirakawa, K. Tamagake and M. Tsuboi, J. Mol. Spectry. 35 (1970) 420.
- [22] P.A. Giguere and I.D. Liu, J. Chem. Phys. 20 (1952) 136.
- [23] T. Tipton, D.A. Stone, K. KuBulat and W.B. Person, J. Phys. Chem. 93 (1989) 2917.
- [24] N. Ohashi, W.J. Lafferty and W.B. Olson, J. Mol. Spectry. 117 (1986) 119.
- [25] J.R. Durig, S.F. Bush and E.E. Mercer, J. Chem. Phys. 44 (1966) 4238.
- [26] E. Catalano, R.H. Sanborn and J.W. Frazer, J. Chem. Phys. 38 (1963) 2265.
- [27] N.N. Greenwood and A. Earnshaw, Chemistry of the elements (Pergamon Press, Oxford, 1984) pp. 489.
- [28] C.-M. Chan, R. Aris and W.H. Weinberg, Appl. Surface Sci. 1 (1978) 360.
- [29] C. Benndorf and T.E. Madey, Surface Sci. 135 (1983) 164.
- [30] E. Tronconi and L. Lietti, Surface Sci. 199 (1988) 43.
- [31] H. Pfnur, D. Menzel, F.M. Hoffmann, A. Ortega and A.M. Bradshaw, Surface Sci. 93 (1980) 431.
- [32] T.E. Madey, H.A. Engelhardt and D. Menzel, Surface Sci. 48 (1975) 304.
- [33] J.E. Parmeter, Y. Wang, C.B. Mullins and W. H. Weinberg, J. Chem. Phys. 88 (1988) 5225.
- [34] P.B. Ryan and H.D. Todd, J. Chem. Phys. 67 (1977) 4787.
- [35] Y. Zhou, S. Akhter and J.M. White, Surface Sci. 202 (1988) 357.
- [36] T. Sasaki, T. Aruga, H. Kuroda and Y. Iwasawa, Surface Sci. 224 (1989) L969.
- [37] F.M. Hoffmann, J. Hrbek and R.A. de Paola, Chem. Phys. Letters 106 (1984) 83.
- [38] J.J. Weimer, E. Umbach and D. Menzel, Surface Sci. 155 (1985) 132.
- [39] R.L.C. Wang and H.J. Kreuzer, Chem. Phys. 177 (1993) 453;
 A. Görling, L. Ackermann, J. Lauber, P. Knappe and N.
- Rösch, Surface Sci. 286 (1993) 26. [40] R.T. Morrison and R.N. Boyd, Organic chemistry, 6th ed.
- (Prentice-Hall, Englewood Cliffs, 1992).
- [41] T.B. Cundari, J. Am. Chem. Soc. 114 (1992) 7879.
- [42] M. Lindroos, H. Pfnür, G. Held and D. Menzel, Surface Sci. 220 (1989) 43.
- [43] R. Dennert, M. Sokolowski and H. Pfnür, Surface Sci. 271 (1992) 1.
- [44] CRC handbook of chemistry and physics, 73rd Ed. (CRC Press, Boca Raton, 1992).

- [45] A.D. Novaco and J.P. McTague, Phys. Rev. Letters 38 (1977) 1286.
- [46] P. Zeppenfeld, K. Kern, R. David and G. Comsa, Phys. Rev. B 38 (1988) 3918.
- [47] H. Schlichting, Doctoral thesis, TU München, 1990.
- [48] M. Sokolowski, Doctoral thesis, TU München, 1992.
- [49] K. Jones, Nitrogen, in: Comprehensive inorganic chemistry, Vol. 2 (Pergamon Press, Oxford, 1973).
- [50] G. Ertl and J. Tornau, Z. Physik. Chem. NF 93 (1974) 109.
- [51] M.P. Kiskinova, Studies in surface science and catalysis, Vol. 70. Poisoning and promotion in catalysis based on surface science concepts and experiments (Elsevier, Amsterdam, 1992).
- [52] M. Grunze, in: Chemical physics of solid surfaces and heterogeneous catalysis, Vol. 4, eds. D.A. King and D.P. Woodruff (Springer, Berlin, 1982).
- [53] G. Ertl, Catal. Rev. Sci. Eng. 20 (1980) 201.
- [54] C.N.R. Rao and G. R. Rao, Surface Sci. Rept. 13 (1991) 221, and references therein.
- [55] J.R. Anderson and M. Boudart, eds., Catalysis science and technology, Vol. 1 (Springer, Berlin, 1981).
- [56] Y.-K. Sun, Y.-Q. Wang, C.B. Mullins and W.H. Weinberg, Langmuir 7 (1991) 1689.

- [57] J.A. Rodriguez, W.K. Kuhn, C.M. Truong and D.W. Goodman, Surface Sci. 271 (1992) 333.
- [58] G. Ertl and T. Giovanelli, Z. Physik. Chem. NF 75 (1971) 137.
- [59] J. Völter and G. Lietz, Z. Anorg. Angew. Chem. 366 (1969) 191.
- [60] E.A. Slaughter and J. L. Gland, J. Vacuum. Sci. Technol. A 10 (1992) 75.
- [61] M.H. Matloob and M. W. Roberts, J. Chem. Res. (1977) 336.
- [62] B. Poelsema, G. Mechtersheimer and G. Comsa, Surface Sci. 111 (1981) 519.
- [63] K. Schwaha and E. Bechtold, Surface Sci. 66 (1977) 383.
- [64] M.L. Colaiani, P. J. Chen and J. T. Yates Jr., J. Chem. Phys. 96 (1992) 7826.
- [65] X.-Y. Zhu, M. Wolf, T. Huett and J. M. White, J. Chem. Phys. 97 (1992) 5856.
- [66] D.F. Johnson, Y. Wang, J.E. Parmeter, M.M. Hills and W.Tl. Weinberg, J. Am. Chem. Soc. 114 (1992) 4279.
- [67] T. Sasaki, T. Aruga, H. Kuroda and Y. Iwasawa, Surface Sci. 276 (1992) 69.
- [68] I.C. Bassignana, K. Wagemann, J. Kuppers and G. Ertl, Surface Sci. 175 (1986) 22.
- [69] E.H. Eyster and R. H. Gillette, J. Chem. Phys. 8 (1940) 369.