Adsorption of Hydrogen Azide on the NaCl(100) Single Crystal Surface. Orientational and Translational Ordering of the HN₃ Monolayer as Revealed by PIRS, LEED and Spectra Simulation

By J. Heidberg*, M. Hustedt, J. Oppermann and P. Paszkiewicz

Institut für Physikalische Chemie und Elektrochemie der Universität Hannover, Callinstr. 3-3A, D-30167 Hannover, Germany

Dedicated to Prof. Dr. Dr. h.c. mult. J. Troe on the occasion of his 60th birthday

(Received March 10, 2000; accepted in revised form September 1, 2000)

Adsorption / Hydrogen Azide HN₃ / NaCl(100) Surface / Polarization Infrared Surface Spectroscopy / Low Energy Electron Diffraction

The adsorption of hydrogen azide HN_3 on NaCl(100) has been studied by means of polarization Fourier transform infrared spectroscopy PIRS and low energy electron diffraction LEED. The well-defined surface was prepared *in-situ* under UHV by cleaving a single crystal with as few dislocations as possible.

Ordered molecular adsorption of HN₃ has been observed. Multiple absorptions of all four molecular vibrations with frequencies between 4000 and 1000 cm⁻¹, all non-degenerate in the gas, are found at 120 K. In particular, a quartet of strongly polarized sharp absorption lines for the asymmetric stretching vibration ν_2 at 2162.8, 2154.0, 2149.2, and 2138.3 cm⁻¹ is obtained, the line at 2162.8 cm⁻¹ being extremely weak in *s*-polarization. Saturation of adsorption, indicating the monolayer, is observed both upon dosing HN₃ in the low coverage range, where island growth is inferred, and desorbing HN₃ from multilayers. No domain orientation appears to be preferred. An activation energy of desorption of $43 \pm 5 \text{ kJ/mol}$ and a pre-exponential factor of $2.6 \times 10^{14 \pm 1.5} \text{s}^{-1}$ were determined.

Isotopic mixture experiments with $H^{14}N_3$ and $H^{14}N^{15}N^{14}N$ reveal that the four absorption lines of the ν_2 vibration are caused first by site splitting due to two energetically inequivalent HN₃-species and second by Davydov splitting due to a strong correlation field between the dynamic dipoles. There are four molecules per adsorbate

^{*} Corresponding author. E-mail: Heidberg@mbox.pci.uni-hannover.de

unit cell: two different pairs of energetically equivalent but translationally inequivalent molecules. Further, two different pairs of NH hydrogen bonds are observed. Tilt angles and intermolecular angles of the adsorbed molecules were determined. The translational symmetry of the adsorbate was derived by LEED. Simulation of the v_2 quartet spectrum based on equations of classical electrodynamics was accomplished yielding the angles, lateral distances and dynamic vibrational couplings within the monolayer. Combining all results we propose a monolayer structure of angularly ordered zigzag chains of HN₃ molecules, where two molecules are linked by a hydrogen bond forming a dimer, while the other weaker hydrogen bond ties the dimers together or to a Cl⁻ surface ion. Two HN₃ dimers make up the $p(2 \times 2)$ monolayer unit cell of 2D space group pg.

1. Introduction

The adsorption on ordered surfaces of ionic solids is a topical field, for which, however, rather little experience is available [1-6]. Most of the powerful techniques of surface science deal with charged particles or ionizing radiation, which cause charging problems and rapid degradation of ionic surfaces. Nevertheless, the adsorption on "salt and rust" has recently attracted much attention. There is an incentive by technology to gain knowledge of ionic insulator surfaces and there is basic interest. Adsorption on salt is expected to be a case of physisorption, which may favor molecular adsorption instead of dissociative chemisorption and, further, reveal conceptual simplicity making the system suitable for fundamental studies [7]. The adsorption on salt is significant in situations ranging from biological chemistry [8,9] to hydrogen atom recombination on interstellar dust grains [10], sea salt aerosols and their reactions with NO_2 and other gases in the troposphere [11], nuclear waste deposition in geological salt domes [12, 13], industrial salt separation by adsorbateinduced contact equilibration and charging [14, 15]. Of fundamental interest are the resonant photodesorption [16–19] and surface aligned photoreactions SAP [20-22], preferably studied on salt surfaces, as shown by Polanyi e.g. for the H₂ desorption from the pulsed laser-induced reaction of H₂S adsorbed on LiF(100) [21]. Narrow distributions of fast and broad distributions of slow H₂ molecules and their angular dependence were observed. The importance of measuring angular structures and the need for trajectory studies was stressed from the beginning. Alkali halides were intentionally chosen as aligning substrates, because the weak molecule-substrate interaction would minimize the complications associated with a rigorous understanding of trajectory studies of the photoreactions. An extremely reactive molecule, explosive, profoundly studied, especially with respect to the quantum states of the system

 $HN_3 = HN + N_2$

in the gas phase and also in the matrix, is hydrogen azide or hydrazoic acid HN_3 [23–28], its standard Gibbs enthalpy of formation at 298 K being +328 kJ/mol [29]. If an ordered monolayer could be prepared, HN_3 would be a candidate for studying surface aligned photoreactions.

Surface reactions of HN_3 were the subject of recent studies. HN_3 was shown to react on silicon(100), (110), (111) [30–32] and GaAs [33] forming nitrides. The reaction of HN_3 on C(100) leading to carbon azide and the nitridation on germanium surfaces were reported [34, 35]. In all these investigations the decomposition of HN_3 and the identification of chemisorbed reaction products was of main interest. Less attention was paid to the structure of the prevailing adsorption system.

Polarization Fourier transform infrared surface spectroscopy (PIRS), in combination with a diffraction technique, LEED or HAS (helium atom scattering) has been applied to observe the localized, as well as the collective, vibrations of simple molecules physisorbed on ionic single crystal surfaces: H₂, CO, CO₂, H₂O, N₂O, COS on NaCl(100) [36–53]; CO, CO₂ and N₂O, H₂O on MgO(001) [54-59], respectively, and others. PIRS has the advantage of being non-invasive, which is necessary for the study of adsorbed reactive, thermolabile and photosensitive HN₃. Moreover, surface selection rules effective on metals and semiconductors do not operate on insulators. Therefore, measurement of surface alignment of molecules is possible by polarized radiation. Isotopic mixture measurements elucidate the collective nature of the observed vibrations by suppressing the dynamic coupling with increasing isotopic dilution [45, 60]. Correlation field or Davydov multiplets may be observed in case of at least two energetically equivalent but translationally inequivalent molecules within the adsorbate unit cell, allowing to determine the absorption cross sections and the lateral distances and angles of the adsorbed molecules [45, 47, 54, 61]. In order to study the translational symmetry of the adsorbate, it can be attempted to employ low energy electron diffraction (LEED), though electron-induced reaction may take place. Using SPA-LEED (spot profile analysis) [62] at extremely low electron current and short measuring time sufficiently high sensitivity is achieved without affecting detectibly the adsorbate [63]. Theoretical studies support the experiments. The spectra of the polarized collective vibrations of physisorbates with ordered structures dominated by long range interactions can be calculated using equations of classical electrodynamics [45, 47, 54] or the quantum mechanical exciton model [61]. Mainly, the dynamic dipole-dipole interactions between the adsorbed molecules are considered, whereas static interactions are introduced by means of so-called singleton frequencies which can be obtained from the isotopic mixture measurements [45, 61, 64-66]. By fitting the calculated to the measured polarized spectra we are able to deduce molecular and structural parameters such as vibrational polarizabilities of the adsorbed species, molecular tilt angles, and the relative positions of the molecules within the adsorbate unit cell.

This work is devoted to the adsorption system HN_3 -NaCl(100). The surface is prepared by cleaving *in-situ* under ultrahigh vacuum a single crystal with fewest dislocations possible. The adsorptive is extremely explosive.

A first characterization of this system has been carried out by means of PIRS [67]. Molecular adsorption of HN₃ on NaCl(100) is observed. The monolayer is indicated by saturation, which is found both upon dosing HN₃ in the low coverage range, where island growth is inferred, and desorbing HN₃ from multilayers. There is a well-defined and highly ordered monolayer at about 120 K. Isotopic mixture measurements will enable us to distinguish between dynamic and static interactions within the adsorbate and to determine the number of energetically inequivalent molecular species in the adsorbate unit cell by means of their singleton frequencies. Using the obtained results an analysis of the polarization dependence of the measured monolayer spectra is performed in order to estimate molecular tilt angles and azimuthal angles within the structure. We present LEED experiments which reveal the translational symmetry of the monolayer. In addition we have calculated the polarized IR spectra in order to clear up structural details. Combining all the information, we propose a structure of the monolayer HN₃ on NaCl(100).

2. Experimental

PIRS

The polarized infrared (PIR) spectra of the adsorbates were recorded by means of a Bruker IFS 113v interferometer with modular optics according to Heidberg, Hoge, Warskulat. The PIRS experiments were performed in a stainless steel UHV chamber equipped with a fully rotatable bath cryostat, ionization and spinning rotor gauges for pressure measurements and a quadrupole residual gas analyzer for the determination of partial pressures. This chamber was flanged to the interferometer and an IR detector compartment equipped with a wire grid polarizer. Both the interferometer and detector compartment were purged with 6 N nitrogen.

The base pressure inside the UHV-chamber was below $2 \cdot 10^{-10}$ mbar. All pressures presented are the uncorrected values of the display of the ionization gauge. Measuring time and current must be small, because HN₃ decomposes on the hot tungsten filament. A $10 \cdot 20 \cdot 20$ mm³ NaCl single crystal of 4 N purity having as few dislocations as possible was attached to an OFHC copper sample holder. The crystal temperature was measured with a NiCr/Ni-thermocouple in contact to one side of the crystal by means of a molybdenum spring and another one attached to the sample holder. Both thermocouples were calibrated *ex situ* at 77 and 273 K. For all FTIR-measurements presented the uncertainty of temperature was 1.0 K; the temperature was kept constant within 0.5 K.

The NaCl single crystals were cleaved in situ under UHV at room temperature with a movable spear-shaped stainless steel blade and an anvil mounted on welded bellows on opposite sides of the chamber to allow adjustment and later retraction of the cleavage device. Two opposite sides of the NaCl-crystal were cleaved to produce two clean NaCl(100) surfaces for infrared transmission experiments.

An InSb-detector for wavelengths from 4000 to 2000 cm⁻¹ and a MCTdetector for wavelengths from 4000 to 1000 cm⁻¹, both operated at 77 K, were used. FTIR-spectra with *s*- and *p*-polarization (electric field vector perpendicular and parallel to the plane of incidence, respectively) were taken at an angle of incidence of $50 \pm 1^{\circ}$ with respect to the surface normal. The spectra discussed were recorded with a resolution of 1.0 and 0.5 cm⁻¹, respectively, 4 term Blackman-Harris-apodization and a zero-filling-factor of 2. Reference spectra were taken from the clean crystal at about 120 K.

Preparation of HN_3 gas was done by mixing H_2SO_4 with dried NaN₃ in a vacuum line followed by fractional distillation of the gas. HN₃ is extremely explosive. Therefore it was diluted with nitrogen and hydrogen, only HN₃ being adsorbed under the conditions applied. Infrared spectra of the gas, recorded instantly after producing, show impurities of less than 0.1% of water and CO₂. Gas admission into the chamber was carefully done through a quartz capillary to avoid decomposition and therefore contamination of the substrate by fragmentation products like ammonia. The capillary aiming straight to the NaCl-crystal, in the plane of IR-incidence about 4 cm apart, admits molecules in a sharp distribution with strong orientation forward as a result from a high ratio pipe length L to radius r (L/r = 50). After calculating the function of distribution the part of molecules which really reaches the crystal surface could be estimated to 35 per cent of the admitted molecules. The number of all molecules dosed was calculated from the difference of pressure in the gas storage compartment. The pressure was measured with a capacity gauge (Baratron) and/or a spinning rotor gauge (MKS). By using the capillary only small amounts of gas were admitted, in order to be able to measure accurately the number of molecules dosed.

After generating the adsorbate on a single side of the NaCl crystal the leak valve for gas admission was closed; the pressure inside the chamber reached $p < 5 \cdot 10^{-10}$ mbar within a few minutes.

LEED

PIRS and SPA-LEED measurements were performed using slightly different experimental setups. The base pressure of the SPA-LEED chamber was below $3 \cdot 10^{-10}$ mbar. $10 \cdot 20 \cdot 20$ mm³ NaCl single crystals of 4 N purity with as few dislocations as possible were cleaved *ex situ* under N₂ atmosphere and then attached to an OFHC copper sample holder. The crystal was annealed in UHV at 440 K for at least 12 h to remove possibly adsorbed residual gas from the surface. To test the quality of the surface a monolayer HN₃-NaCl(100) was prepared. IR spectra recorded in the range of the asymmetric NNN-stretching vibration of HN₃ (ν_2) show no significant differences to spectra obtained from NaCl(100) surfaces cleaved *in situ* under UHV. Values of peak frequencies, integrated absorptions and widths at half maximum (FWHM) are the same within the accuracy of measurement.

The LEED measurements were performed with a high resolution Leybold SPA-LEED instrument (spot profile analysis of LEED according to Henzler) [62]. The diffraction patterns presented were taken at an electron energy of 69 eV. After the alignment of the LEED system a diffraction pattern of the clean NaCl(100) surface was measured. During admission of HN_3 the intensity of the (0 0) spot was recorded as a function of time. After saturation had been reached, a complete LEED pattern of the adsorbate was taken. Another method to obtain a LEED pattern of the adsorbate was also employed: after preparing the adsorbate under IR-control the sample was moved into the plane of measurement for performing the LEED experiment.

3. Experimental results – PIRS

Generating the adsorbate under PIRS control

To adsorb HN₃ on the NaCl(100) surface the crystal was cooled to 120 K and the HN₃-gas, diluted with nitrogen and hydrogen in the ratio 1 HN₃ to 13 dilutant molecules, was dosed carefully through a capillary to one side of the NaCl-crystal only. Polarized FTIR-spectra were recorded during admission of HN₃-gas; the integrated absorption in the range of the asymmetric NNN-stretching vibration of gaseous HN_3 (ν_2), which is non-degenerate in the gas (2140.3 cm⁻¹), was measured after each quantity, adequate to one dose equivalent $(3.7 \cdot 10^{15} \text{ molecules})$. Fig. 1 shows the growth of an adsorbate layer at constant temperature of 120 K in the range of the v_2 mode. Its integrated absorption A_{int} as a function of the dosed HN₃-molecules is shown in Fig. 2. Reaching constant integrated absorption after dosing some $4.5 \cdot 10^{16}$ molecules indicates saturation coverage, which is defined to be the monolayer. As the spectral line widths and frequencies do not change upon dosing, 2D island growth is inferred. A quartet of sharp absorption bands (FWHM about 1.8 cm^{-1}) for *p*-polarization and a triplet for *s*-polarization are observed indicating the existence of a highly ordered adsorbate. To clear up, whether the observed multiplet is caused by a correlation field, isotopic mixture experiments were performed, which are described in the Sect. 4. As indicated their results are important for the determination of the adsorbate structure.

The same state of saturation was also reached upon integral dosing at 120 K and $p(\text{HN}_3) = 5 \cdot 10^9$ mbar within about 30 min.

Saturation is also found by desorption of multilayers: sublimation at 123 K leads to the same spectral features, clearly separable from the spectrum of the multilayers with its additional absorptions (see below in this Sect. 3 for a more complete description).



Fig. 1. Polarized infrared spectra of HN₃ adsorbed on NaCl(100) in the range of the v_2 mode. The surface was prepared by cleaving *in-situ* under UHV. The spectra show the growth of the adsorbate at constant temperature of 120 K as a function of the number N of molecules dosed. The multiplet structure does not change with N indicating island growth. Angle of incidence 50°, resolution 1.0 cm^{-1} , 4 term Blackman-Harris apodization.

PIRS of the monolayer HN_3 adsorbed on the NaCl(100) single crystal surface

Polarized FTIR-spectra in the range 3300 to 1100 cm^{-1} were taken at monolayer coverage at 120 K. As shown in Fig. 3 all gas phase absorptions (ν_1 to ν_4) in this range, all being non-degenerate, could be observed in the adsorbate,



Fig. 2. Integrated absorption A_{int} of the v_2 bands of adsorbed NH₃, shown in Fig. 1, as a function of the number N of HN₃ molecules dosed by means of a quartz capillary, about 35% of N striking the NaCl(100) surface. T = 120. The gas dosed contained N₂, H₂ and 7.7 mol % HN₃. The measured values fit to a sigmoidal function in concert with island growth.

too. In the following the different absorption bands of the adsorbate will be discussed:

1. Symmetric NH-stretching mode (v_1 , gas phase frequency 3338.9 cm⁻¹) [68]

This absorption mode shows two rather broad bands at 3208 (*A*) and 3166 (*B*) cm⁻¹, both red shifted with respect to the gas phase value. The large red shifts, 131 cm⁻¹ for band *A* and 173 cm⁻¹ for band *B*, as well as the shape of the bands, especially the FWHM which is about 15 cm⁻¹, indicate strong hydrogen bonding within the adsorbate. The integrated absorption A_{int} of the *A*-band (*B*-band) both in *p*- and *s*-polarization is about 1/3 (1/2) of the sum of the integrated absorptions of the *E* and *F* bands (*G* and *H* bands) (see below). The small integrated absorption and the large width can be the cause, why no Davydov splitting is observed at 120 K.

2. Asymmetric NNN-stretching mode (v_2 , gas phase frequency 2140.3 cm⁻¹) [69]

As already shown above, in the range of the v_2 mode a quartet in *p*-polarization and a triplet in *s*-polarization, respectively, were observed in the adsorbate phase. Four (three) sharp absorptions are obtained at 2162.8 (*C*) (not in *s*-polarization), 2154.0 (*D*), 2149.2 (*E*), and 2138.3 cm⁻¹ (*F*). The integrated absorptions are in *p*-polarization 0.0115 (*C*), 0.0112 (*D*), 0.0039 (*E*), 0.0213 (*F*) cm⁻¹, and in *s*-polarization 0.0205 (*D*), 0.0081 (*E*), 0.0326 (*F*) cm⁻¹. Three frequencies are blueshifted with respect to the gas



Fig. 3. Polarized infrared spectra of the monolayer HN_3 adsorbed on the NaCl(100) single crystal surface in the range 3300 to 1100 cm^{-1} . All gas phase bands (ν_1 to ν_4), all being non-degenerate, are observed in the adsorbate. Angle of incidence 50°, resolution 0.5 cm⁻¹, 4 term Blackman-Harris apodization.

phase value, one frequency is weakly redshifted. All frequencies are close to the gas phase value as expected for a physisorption system, that means decomposition can be excluded. The sharpness of the bands (FWHM of band C and D 1.6 cm⁻¹, E 2.0 cm⁻¹ and F 1.7 cm⁻¹), which show Lorentzian lineshape, indicates the presence of a highly ordered adsorbate structure. The integrated absorption in the spectrum with *p*-polarized light (A_p) is 0.049 cm⁻¹ and in that with *s*-polarized light (A_s) is 0.063 cm⁻¹; these wellreproducible values will be taken for the monolayer absorption. The accuracy of the A_{int} -values of the v_2 is about 10%. The lack of band C in *s*-polarization indicates the existence of an absorption mode perpendicular to the surface. This mode can be assigned to an in-phase (symmetric) vibration considering the simple theory taking into account the relative electric fields at the surface for the applied angle of incidence. This model based on the classical Fresnel formulae predicts a highest possible A_s/A_p -ratio of 1.67 as it is calculated for the band D, which therefore can be assigned to the corresponding out-of-phase (anti-symmetric) mode parallel to the surface. From the A_s/A_p -ratio of the two remaining absorptions E and F we obtain modes nearly parallel to the surface. Therefore, they are attributed to adsorbed HN₃ molecules having their NNN-chain nearly flat on the surface. The high intensity of this absorption and the convenient spectral range with a high signal to noise ratio renders this absorption favorable for further accurate investigations.

3. In-plane HNN-bending mode (v_3 , gas phase frequency 1266.6 cm⁻¹) [70]

For the bending mode ν (HNN) two broad absorptions of low intensity at 1294 and 1262.0 cm⁻¹ were observed. One absorption is blueshifted and the other slightly redshifted with respect to the gas. Some features of these absorptions resemble those of the ν (HN) mode: the large FWHM of 16 cm⁻¹ and 9 cm⁻¹ (for the band at higher frequency), respectively, as well as the frequency split of about 32 cm⁻¹ may indicate the participation of the H-atom in hydrogenbonding within the adsorbate.

4. Symmetric NNN-stretching vibration (v_4 , gas phase frequency 1147.4 cm⁻¹) [70]

In the range of ν_4 we observed three absorptions at 1160.4, 1173 and 1192 cm⁻¹. The spectral features differ obviously from those of ν_2 concerning intensities and FWHM (4.5, 4, and, about 12 cm⁻¹). With respect to the low signal to noise ratio a quantitative analysis of the spectra is too uncertain compared with the ν_2 bands.

Domain distribution as determined by PIRS

To determine the domain distribution and orientation of the adsorbate unit cells, the polarization angle was varied from 0° to 180° in steps of 15° at an angle of IR-incidence of 0° with respect to the surface normal (azimuthal incidence). The observed FTIR-spectra do not show any remarkable variations of the band intensity in the range of the ν_2 vibration (ν_2 -multiplet). No preferred orientation of domains is inferred.

Desorption kinetics of the adsorbate as determined by PIRS

To study the desorption kinetics of the adsorption system HN_3 -NaCl(100) equal quantities of HN_3 gas (ten times more than necessary to generate the state of saturation at 120 K) were admitted at five different substrate temperatures (130.9, 133.0, 134.9, 137.2, and 139.5 K), but not enough to prepare a multilayer film. Admission of the gas was stopped (t = 0) and immedi-



Fig. 4. Decrease of the integral absorption A_{int} of the *s*-polarized v_2 bands of the adsorbate during desorption at five different temperatures. Measured values fit to a sigmoidal function.



Fig. 5. Logarithm of the rate coefficient K_{des} derived from Fig. 4 in the coverage range at $\Theta = 0.3$ as a function of the reciprocal absolute temperature *T*. From the Arrhenius-plot the activation energy of desorption E_d and the frequency factor *A* given in the figure are obtained.

ately FTIR-spectra were recorded during the desorption of HN₃ from the NaCl surface. Fig. 4 shows the decrease of A_{int} in the range of the v_2 mode with time for these five temperatures. In all cases a sigmoidal curve shape was obtained indicating a complex desorption mechanism. At coverage around 0.6 zero order kinetics was found, expected for desorption from a 2D island–2D lattice gas equilibrium. A first order desorption kinetics was determined around the coverage $\Theta = 0.3$. The dependence of the rate coefficients for $\Theta \cong 0.3$ on temperature is shown in an Arrhenius-plot (Fig. 5). The activation desorption energy E_d and the frequency factor A were calculated to be $E_d = 43 \pm 5 \text{ kJ/mol}$ and $A = 2.6 \cdot 10^{14\pm1.5} \text{ s}^{-1}$. The value of E_d should be in the range of the isosteric heat of adsorption which we can not measure at first hand. Nevertheless,

there is often a good agreement with the values of E_d directly measured under conditions both of equilibrium and of non-equilibrium [71]. With these results we estimated the stability of the physisorption system expressed through the half life time $t_{1/2}$ of the adsorbed HN₃-molecules. At T = 120 K we calculated $t_{1/2}$ to be greater than 4.7 h which means ideal condition for preparation of the adsorbate; at T = 110 K $t_{1/2}$ will be greater than ten days (242.2 h) and adsorption (physisorption) can be considered as almost irreversible. The high activation desorption energy $E_d = 43$ kJ/mol leads to the assumption of strong hydrogen bonds causing either lateral interactions or interactions between HN₃-molecules and surface ions (Cl⁻). Mass spectra recorded during desorption show intact HN₃-molecules also proving molecular adsorption on NaCl(100).

PIRS of multilayers of HN₃ adsorbed on NaCl(100)

In addition to the frequencies in the monolayer both for *p*- and *s*-polarized light several new absorptions appear for HN₃-multilayers. Upon warming up the multilayers from 103 to 123 K the integrated absorption of the v_2 bands remained constant until T = 118 K was reached; at this temperature A_{int} began to decrease, as a consequence of sublimation. This result shows that the interactions of molecules in the solid phase (multilayer) must be weaker than those in the adsorbate (monolayer). Up to 130 K no remarkable desorption of the adsorbate was detected within minutes (compare with the desorption experiments of the adsorption system). The sublimation of HN₃ multilayers



Fig. 6. *s*-Polarized infrared spectra of HN₃ multilayers adsorbed on the NaCl(100) single crystal surface in the range of the ν_2 mode during sublimation at T = 123 K. Two minutes delay *Dt* between consecutive spectra. Angle of incidence 50°, resolution 1.0 cm⁻¹, 4 term Blackman-Harris apodization.



Fig. 7. (a) Integral absorption A_{int} of the v_2 spectra shown in Fig. 6 versus time *t*. (b) Plot of the logarithm of A_{int} as function of time *t* reveals a sublimation kinetics of first order with the rate coefficient $k_1 = 3.9 \cdot 10^{-3} \text{ s}^{-1}$.

consisting of about 4 monolayers was investigated at constant temperature more closely by inspecting the behavior of the three to four additional bands and shoulders, shown in Fig. 6. It is clearly seen that the sublimation of multilayers from the NaCl(100) surface led to the same spectral features as are observed in 2D island growth: Many more HN₃ molecules were admitted to the sample than necessary to generate the saturated phase at 123 K. During the immediately starting sublimation of the HN3-multilayers FTIR-spectra with spolarization were recorded almost continuously (pause of two minutes between two spectra) and the integrated absorption was measured for each spectrum in the range of the ν_2 . After 20 min a stable coverage was reached (Fig. 7a). This state of the adsorption system corresponds to the monolayer obtained by admitting certain quantities of HN₃ molecules. The kinetics of this isothermal process can be well described by a rate equation of first order, while zero order kinetics was expected. In first order kinetics the change of A_{int} as a function of time is directly proportional to the integrated absorption itself: $r_{\rm d} = dA_{\rm int}/dt = -k_1 \times A_{\rm int}$. From the plot logarithm $A_{\rm int}$ versus time (Fig. 7b) the rate coefficient of sublimation $k_1 = (3.9 \pm 0.4) \cdot 10^{-3} \text{s}^{-1}$ was derived. Thus, desorption from multilayers proceeds within minutes, desorption from the first layer within hours at 123 K showing the strength of the HN₃–NaCl interaction.

Conclusions from PIRS

We have shown that HN₃ adsorbs molecularly on NaCl(100) generating a highly ordered adsorbate structure. 2D island growth up to a defined saturation coverage was observed, which we assume to be the monolayer coverage. This adsorption phase is clearly distinguishable from multilayers. Sublimation of multilayers at 123 K resulted in the same spectral features as obtained from 2D island growth. Between 4000 and 1000 cm⁻¹ we found two rather broad absorptions in the range of the v_1 NH stretch mode, strongly red shifted, as well as in the range of the ν_3 NNH bending mode indicating strong hydrogen bonding within the adsorbate. Further we observed four strongly polarized sharp bands in the range of the ν_2 asymmetric NNN stretch mode which allows a first assignment of the observed bands and we derived first structural information from these. Three less resolved absorptions in the range of the v_4 symmetric NNN stretch mode were detected. The rather high activation energy of desorption, which was determined to be (43 ± 5) kJ/mol, supports the assumption of hydrogen bonds within the adsorbate, possibly important for the formation of the adsorbate structure.

In the next section, dealing with the determination of the adsorbate structure, systematic isotopic mixture experiments were carried out to clear up the number of energetically different adsorption species. Also LEED investigations could be performed in order to determine the translational symmetry of the adsorbate. Complete spectra simulations were achieved providing additional information which allows to propose a model for the adsorbate structure.

4. Isotopic mixture experiments with $H^{14}N_3$ and $H^{14}N^{15}N^{14}N-PIRS$

Site and Davydov splittings. Energetically inequivalent HN_3 species I and II

All four fundamental vibrations in the range between 3500 and 1100 cm^{-1} known from the gas phase were observed in the adsorbate. For the further discussion only the very intense absorption multiplet of the v_2 mode which shows strong polarization dependence will be of interest.

To verify, whether the quartet of the ν_2 is caused by a correlation field splitting (Davydov-splitting) due to long range dynamic dipole-dipole coupling of energetically equivalent but translationally inequivalent molecules in a highly ordered adsorbate system, an isotopic mixture experiment was performed.

Isotopic mixtures of $H^{14}N_3$ and $H^{14}N^{15}N^{14}N$ with different compositions were prepared in the gas inlet of the UHV-system and admitted on the NaCl(100) surface; spectra of these mixtures at monolayer coverage were recorded at about 120 K. Fig. 8 shows *p*- and *s*-polarized transmittance spec-



Fig. 8. *p*- and *s*-polarized transmittance ν_2 spectra of HN₃-NaCl(100) at monolayer coverage. Isotopic mixtures with various fractions of H¹⁴N₃: $x({}^{14}N_3) = \Theta(H^{14}N_3)/(\Theta(H^{14}N^{15}N^{14}N) + \Theta(H^{14}N_3))$. T = 120 K, angle of incidence $50 \pm 1^\circ$, resolution = 1.0 cm⁻¹. Zerofilling-factor = 2; 4 term Blackman-Harris apodization.

tra of these mixtures with varying the ratios of the isotopic species, stated as the mole fraction x (${}^{14}N_3$) of the H ${}^{14}N_3$ isotope. At *p*-polarization the splitting between the bands C and D and the bands E and F diminishes with decreasing ratio of x ($^{14}N_3$). For the low-frequency band F a significant blue shift is observed, whereas for the bands C and D at higher frequencies a weak red shift and a weak blueshift, respectively, are found. The same behavior is observed for the ¹⁵N-isotope. In both cases only two absorptions are obtained for the minor component in the very diluted state. For s-polarization an analogous change in the appearance of the spectra is observed. An intensity transfer between the two isotopic species comparing the mixture of the gas phase with that of the adsorbate could not be found within the experimental uncertainty. The splitting into a multiplet does not exist for very diluted isotopic components because they are surrounded by oscillators of different frequency to which the dynamic coupling becomes very ineffective. Instead we observe as many bands as energetically different species of a single isotope exist within the adsorbate unit cell.

The dependence of the peak frequencies on the partial coverage of the $H^{14}N_3$ isotope is presented in Fig. 9. The frequencies of the bands were plotted as a function of $x ({}^{14}N_3)$. Within the error limits both bands *C* and *D* as well as the bands *E* and *F* coalesce in the infinite-dilution limit. By extrapolation to this point we obtain the singleton frequencies of the energetically inequivalent



Fig. 9. Peak frequencies of the ν_2 bands of the H¹⁴N₃ isotope at monolayer coverage as a function of the mole fraction $x^{14}N_3$. Peak frequencies are obtained from the spectra in Fig. 8. The labeling of the absorption lines (*C*, *D*, *E*, and *F*) follows the denotation of Fig. 3.

adsorption species within the unit cell. For the $H^{14}N_3$ isotope we find 2156.9 and 2149.7 cm⁻¹ and for the $H^{14}N^{15}N^{14}N$ isotope 2114.6 and 2107.8 cm⁻¹, respectively.

These experimental data show that the bands C and D as well as the bands E and F represent correlation field doublets due to long range dipole–dipole-interactions in an ordered adsorption structure. Therefore each adsorbate unit cell contains at least four molecules which are arranged in two different groups

of energetically equivalent but translationally inequivalent molecules (species I and II). From dosage experiments and the calculation of the local requirement of one HN_3 molecule from its 3D-density it can be stated that no more than four molecules are reasonable to suppose in the unit cell.

The tilt angle ϑ of the observed transition dipole moments with respect to the surface can be determined from the ratio of integrated absorption for *s*- and *p*-polarization A_s/A_p . This determination is based on a geometrical calculation taking into account the relative electric fields at the surface as calculated for the applied angle of incidence using the classical Fresnel formulae and the optical constants of the substrate (n = 1.52 for NaCl at 2000 cm⁻¹) [72]. The C_{4v} symmetry of the substrate NaCl enters the calculation by assuming a statistical distribution of the adsorbate domains with respect to the <010> and <001> azimuthal crystal directions. For NaCl and an angle of incidence $\alpha = 50^{\circ}$ this model predicts a highest possible A_s/A_p -value of 1.7 corresponding to $\vartheta = 0^{\circ}$, i.e. a transition dipole moment parallel to the surface. The tilt angles of three of the observed transition dipole moments are found to be almost parallel to the surface within the error limits and the one corresponding to band *C* (2162.8 cm⁻¹) is perpendicular to the surface.

For an arrangement of two energetically equivalent but translationally inequivalent molecules per unit cell (species I or II) one component of the resulting IR-doublet represents a collective in-phase (symmetric) vibration v^+ the other one an out-of-phase (anti-symmetric) vibration v^- . In a first approximation this is given by the vector addition of the transition dipole moments $\vec{\mu}_1, \vec{\mu}_2$ of the two molecules, assuming that there is no dynamic coupling between the different species:

$$\sqrt{2}\vec{\mu}^{+} = \vec{\mu}_{1} + \vec{\mu}_{2} \sqrt{2}\vec{\mu}^{-} = \vec{\mu}_{1} - \vec{\mu}_{2} .$$

The factor $\sqrt{2}$ is introduced in order to keep the overall integrated absorption constant, which is proportional to the square of the magnitude of the transition dipole $|\vec{\mu}|^2$. Since the components normal to the surface of the molecular transition dipole moments always cancel each other in case of the out-of-phase vibration the corresponding tilt angle ϑ^- must be 0°. The tilt angle ϑ^+ of the transition dipole moment of the in-phase vibration depends on the intermolecular angle φ , which is defined as the angle between the projections of the molecular axes of the two translationally inequivalent molecules onto the surface in the adsorbate unit cell. If the molecules are oriented antiparallel then ϑ^+ becomes 90°; if φ approaches 0° then ϑ^+ approaches the molecular tilt angle ϑ . Using a simple geometric consideration φ can be estimated from ϑ and ϑ^+ via $\varphi = 2 \cdot \operatorname{arc} \cos(\tan \vartheta/\tan \vartheta^+)$.

As the tilt angle of the transition dipole moments corresponding to the IR bands *C* and *D* are 90° and close to 0°, respectively, these bands can be assigned to the in-phase (band *C*) and the out of phase vibration (band *D*) of the

correlation field doublet of species II. With these results, the tilt angle ϑ_{II} of about $(25 \pm 5)^{\circ}$ can be taken for the tilt angle of the NNN-chain to the surface because the transition dipole moment of the ν_2 mode is nearly within the NNN-axis. The intermolecular angle φ_{II} has to be 180°, explained by the lack of the *s*-polarized IR signal for the in-phase mode; therefore species II is represented by two anti-parallel molecules in the adsorbate unit cell.

The tilt angles $\vartheta(E)$ and $\vartheta(F)$ are both close to 0° corresponding to an orientation of the NNN-chain of the species I parallel to the surface. An assignment which band corresponds to the in-phase or to the out-of-phase vibration is not possible. The intermolecular angle φ_{I} can be estimated to be $(50 \pm 5)^{\circ}$.

The two bands *A* and *B* of the N–H stretching vibration (ν_1) confirm the existence of two different adsorbate species as well. The low frequency NH band *B* is assigned to species I, being the H bond donor species in the dimer in accord with the spectrum of the HN₃ dimer in the nitrogen matrix. On the same ground the NH band *A* is attributed to the acceptor species II. (See end of Sect. 6). Inspecting the A_s/A_p -ratio of the ν_1 absorptions we could determine the tilt angle of the N–H-bond to the surface. For species I and II we calculated the tilt angle ϑ to be 7° ± 10° and 13° ± 5, respectively. Probably as a result of the weakness and the broadness of the ν_1 absorptions (FWHM 9 and 15 cm⁻¹, respectively) we do not see an expected correlation field at 120 K. Due to the C_s symmetry of the HN₃ we can now propose the orientation of the HN₃-plane (molecule) with respect to the NaCl(100) surface. Fig. 13 (see below) gives an impression of the local adsorbate geometry of the two HN₃-species.

5. Experimental results – LEED

Adsorbate preparation. Monolayer lattice symmetry $p(2 \times 2)$

The LEED pattern obtained from the uncovered NaCl(100) surface is shown in Fig. 10. The well known NaCl(100) 1×1 pattern is distinctly observed; it should be pointed out that the (*h* 0)- and the (0 *k*)-spots (with *h*, *k* = 1, -1) are extinguished at this electron energy (69 eV). Though, this energy was chosen to have a compromise of low charge effects and high intensive substrate spots.

For the preparation of a HN₃ monolayer via integral dosing (p(HN₃) = $5 \cdot 10^{-9}$ mbar), a sigmoidal monotonous intensity decrease of the (0 0) spot with time was found and saturation occurred after about 20 min (see Sect. 3); no significant minimum was observed; this indicates island growth of the adsorbate domains supporting the result of the dosing experiments under IR-control in Sect. 3 where island growth has already been seen. It is assumed that a monolayer HN₃ on NaCl(100) was generated corresponding to the state of saturation in IR-experiments. Estimating the number of molecules hitting the surface at a HN₃ partial pressure of $5 \cdot 10^{-9}$ mbar two 'monolayers' could have been generated within 1200 s, assuming the sticking coefficient being S = 1. This should be seen as an upper limit for the number of HN₃ molecules



Fig. 10. (left) LEED-pattern of the uncovered NaCl(100) single crystal surface. Electron energy 69 eV. (1 × 1) pattern with missing (1 0)-spots, which are extinguished at the electron energy of 69 eV. Sample temperature 120 K, $p = 2.5 \cdot 10^{-10}$ mbar.

Fig. 11. (right) LEED-pattern of HN₃ adsorbed on the NaCl(100) single crystal surface at saturation (monolayer) coverage showing a $p(2 \times 2)$ superstructure. Sample temperature 119 K, $p = 1 \cdot 10^{-9}$ mbar. Electron energy 69 eV.

adsorbed on the NaCl(100) surface. The obtained superstructure pattern of HN_3 -NaCl(100) are poorly resolved indicating the existence of a $p(2 \times 2)$ superstructure. Taking into account the long SPA-LEED measurement we assume that the electrons hitting the adsorbate lead to significant decomposition of the HN_3 -molecules and therefore disturbance of the highly ordered adsorbate.

In contrast to the integral dosing method the monolayer HN₃ on NaCl(100) was generated in a further experiment under IR-control, where capillary dosing was chosen as described in the Sect. 2. Then the sample was moved into the SPA-LEED plane and a diffraction pattern was recorded. The LEED pattern of the adsorbate structure is shown in Fig. 11. Superstructure spots related to a $p(2 \times 2)$ structure can be clearly seen. Spots at half indexed sites show intensities below 360 cps; intensities of (h k) spots (h, k = 1, 0, -1) are observed between 1000 and 14 000 cps – the latter intensity for the most intense, directly reflected (0 0) spot. Due to the low intensities of the superstructure spots at half indexed sites, which were just above the noise, a closer investigation was not yet possible.

The $p(2 \times 2)$ adsorbate unit cell is four times larger than the NaCl(100) (1×1) surface unit cell. Taking into account the density of condensed hydrogen azide one molecule HN₃ ($\rho_1 = 1.127 \text{ g/cm}^3$) has a local requirement of about 15.9 Å² in the surface plane [73]. This is nearly the dimension of the NaCl (1 × 1) surface unit cell (15.7 Å²). Therefore we suppose one HN₃ molecule per NaCl ion pair leading to four HN₃ molecules per adsorbate unit cell. This assumption is in concert with the estimation of the maximum cover-

age of the substrate from the dosing experiment where we assumed a sticking coefficient S = 1 to calculate the upper limit of adsorbed molecules (two HN₃ molecules per NaCl ion pair). The more probable average coefficient $S \approx 0.5$ supports the assumption of four molecules within the adsorbate unit cell in accordance with the results of the isotopic mixture experiment.

From the 17 two-dimensional space groups we can exclude those 9 groups with symmetry elements such as threefold and sixfold axis of rotation or inversion. The space groups p1, p2, pm, pg, pmm, pmg, p4, and p4m are of importance for the simulation of the IR-spectra.

6. Summary of the experimental results

In order to get a basis for the following theoretical investigations a short summary of the experimental results concerning the adsorbate structure is given in this section.

By means of LEED we have found a commensurate $p(2 \times 2)$ structure with a 2D lattice constant of 7.91 Å for the saturation phase of HN₃-NaCl(100). Eight of the seventeen existing 2D space groups (p1, p2, pm, pg, pmm, pmg, p4, and p4m) are in agreement with the observed LEED pattern. Further reduction of the number of possible structures can be achieved by considering the obtained IR-results. The IR-spectra of the asymmetric stretching vibration v_2 at saturation coverage show a well resolved polarization dependent multiplet with four absorption bands at 2162.8 cm⁻¹ (C), 2154.0 cm⁻¹ (D), 2149.2 cm⁻¹ (E), and 2138.3 cm⁻¹ (F). The line widths of all the bands are between 1.5 and 2.5 cm⁻¹ depending on the quality of the substrate. These spectral features already indicate the existence of a well-ordered adsorbate structure. Furthermore the number of absorption bands shows that there are at least four HN₃-molecules per unit cell. Taking into account the dosage experiments described in Sect. 3 and the density of condensed HN₃ which is 1.127 g/cm^3 we infer that the unit cell contains exactly four HN₃-molecules that means one molecule per Na⁺Cl⁻ ion pair. The ratio of the integrated absorptions at s- and *p*-polarization obtained from the spectra measured at an angle of incidence of 50° is zero for band C. This observation corresponds to an induced dipole moment perpendicular to the NaCl(100) surface. However, the A_s/A_p ratios for the remaining three bands D, E, and F are about 1.7 which means that the corresponding dipole moments are parallel to the surface considering the nearly statistical distribution of adsorbate domains measured at normal incidence. The isotopic mixture measurements now reveal two different singleton frequencies (2156.9 cm⁻¹ and 2149.7 cm⁻¹) which means that there are two energetically inequivalent HN₃-species in the unit cell. As two of the four bands of the spectra of the isotopically pure HN₃ seem to belong to one singleton frequency, respectively, we infer that the unit cell contains two energetically inequivalent pairs of energetically equivalent but translationally inequivalent HN₃-molecules which correspond to two superimposing correlation field or 'Davydov' dublets in the IR-spectra assuming that there is no interaction between the different species. According to this the polarization dependence of the absorption bands leads to a tilt angle ϑ of about 25° with respect to the surface and an antiparallel orientation for the molecules of species II while the molecules of species I are arranged nearly parallel to the surface and enclose an angle φ of about 50°. Here molecular orientation means the orientation of the observed ν_2 transition dipole moment which is nearly parallel to the NNNchain of HN₃. It should be mentioned that the positions of the hydrogen atoms cannot be specified by analyzing the ν_2 -spectra.

Combining all the information mentioned above we conclude that only three of the existing 2D space groups, that is *pg*, *pm*, and *pmg*, represent possible symmetries for the adsorbate structure because pure two-fold and four-fold symmetries can be excluded.

Additional IR-spectra of matrix isolated HN₃ molecules show besides the monomer absorptions a band in the range of the v_1 at 3171 cm⁻¹ as well as two sharp bands in the range of the v_2 at 2142 and 2162 cm⁻¹, respectively, which can be attributed to dimer bands in good agreement with previous results reported by Pimentel *et al.* [74]. These spectra can be interpreted as two HN₃ molecules linked in head-to-tail or head-to-head orientation forming the dimer. We prefer the latter configuration taking into account our calculations of the potential energy of the HN₃ dimer and calculations of the electron density of the HN₃ molecule which shows the highest density at the N atom forming the HN bond ('head' of the molecule, N_α) [75]. Therefore the hydrogen bond in the dimer most likely links two HN₃ molecules in the head-to-head configuration.

7. PIRS – Spectra Simulations

Long range dynamic dipole-dipole coupling

In order to calculate vibrational spectra we have to determine the absorption cross sections σ_{IR} of the adsorbed molecules as a function of the wavenumber. Using our simple model based upon the equations of classical electrodynamics the cross section is proportional to the imaginary part of the dot product of the induced dipole moment \vec{p}_{ind} and the external electric field \vec{E}_{ext} at the crystal surface which can be derived from the Fresnel equations for reflectivity and transmittance [76]. The induced dipole moment of a molecule is given by the product of its dynamic polarizability α_{dyn} and the vector of the local electric field \vec{E}_{loc} at the site of the molecule considered which is caused by the sum of the external electric field mentioned above and the field of the adjacent dipoles. The latter is the dynamic dipole–dipole coupling that results in the observed collective vibrations. The dynamic polarizability is a tensor which is usually specified in molecular coordinates where only the diagonal elements are unequal to zero. The different components of the polarizability tensor consist of

the electronic polarizability α_e which is almost independent of the wavenumber in the infrared region and of the vibrational polarizability α_v described by a complex Lorentzian function. If there are *N* molecules on the surface \vec{p}_{ind} will be a function of N-1 dipole moments with 3 components, respectively. Therefore we have to solve a system of 3N equations. Taking into account the translational symmetry in an ideal adsorbate the system of 3N equations can be reduced to a system of 3M equations where *M* is the number of molecules in the adsorbate unit cell.

The concept of the computer program which was developed to simulate IR spectra of different highly ordered adsorbates is to fit the calculated to the measured spectra by varying several structural and molecular parameters. For the first attempts we have assumed the translational symmetry pg (with glide planes) which has been reported for the system CO₂-NaCl(100) [45–47]. Recently, simulations based upon the 2D space groups pmg (with glide planes, mirror planes perpendicular to them and two-fold rotation axes) as reported for CO-NaCl(100) [40] and pm (with mirror planes) have been performed. The results for these symmetries have to be verified in further investigations.

The parameters varied during the optimization procedures are the angles ϑ and φ , the vibrational polarizabilities α_v , the difference *d* of the distances of the species I and II perpendicular to the single crystal surface and a certain number of structural parameters (three in case of *pg* and *pm*, one in case of *pmg* symmetry) which describe the positions of the molecules within the unit cell. The line width parameters Γ_0 and the singleton frequencies $\tilde{\nu}_0$ mentioned above are introduced as constants. As the electronic polarizabilities α_e are not known for HN₃ the corresponding values of CO₂ (4.0 Å³ for the *x*-components and 2.0 Å³ for the *y*- and *z*-components [73]) are used especially since the electronegativities and electronic configurations are similar.

In order to determine the quality of the simulation the quadratic deviations of peak positions and intensities from the corresponding values of the measured p- and s-polarized IR spectra are calculated and added to an optimization criterion. In Fig. 12 the results of four optimization processes are compared with measured spectra. It should be pointed out that the simulations were performed by averaging the adsorption on the front side and on the back side of the single crystal, for the model used to calculate the electric fields at the crystal surface apparently does not describe the conditions on a single side correctly whereas summation supplies useful values for a single side as well as for both sides.

The spectra marked with 'exp.' (Fig. 12) were recorded at a temperature of about 123 K (instrumental resolution 1.0 cm^{-1} , for further parameters see Fig. 1). The spectra marked with letter '*pg*' are calculated spectra (resolution 0.2 cm^{-1}) which correspond to the 'best fit' assuming the translational symmetry *pg*. The correspondence to the measured spectra is obvious. It should be remarked that according to the simulations there are four bands at *s*-polarization as a consequence of the vibrational coupling between the energetically inequivalent molecular species. This is in contrast to the simple model used to



Fig. 12. Measured (exp.) and calculated (*pg, pmg,* and *pm*) *s*-and *p*-polarized absorption spectra of the monolayer $H^{14}N_3$ adsorbed on NaCl(100) in the range of the ν_2 mode. Angle of incidence 50°. Site and Davydov splitting due to the long range correlation field. Best fit reached for the 2D space group *pg*, separation of energetically inequivalent HN_3 in the direction normal to the surface $d \le |3|$ Å.

determine the tilt angles and intermolecular angles mentioned in Sect. 4. Finally the spectra marked with 'pmg' and 'pm' have been calculated assuming the translational symmetries pmg and pm, respectively. The 'best fits' shown are bad compared to the spectra obtained for pg symmetry (the peak frequencies can be reproduced for pmg and pm, but the intensities not at all). Therefore we infer that structures with pmg and pm symmetries can be excluded.

The important simulation parameters which have been determined assuming pg symmetry are the tilt angle $\vartheta = 45^{\circ}$ of the molecules of species II, the intermolecular angle $\varphi = 72^{\circ}$ of species I, the vibrational polarizabilities $\alpha_{vx1} = 0.44 \text{ Å}^3$ (species I) and $\alpha_{vx2} = 0.20 \text{ Å}^3$ (species II), and the distance between the species d = -3.0 Å. Taking into account the three parameters which describe the molecular positions in the unit cell we are able to propose a reasonable pg adsorbate structure which is shown in Fig. 13 as a projection of the HN₃-molecules onto the single crystal surface.

The HN₃-molecules seem to form chains oriented parallel to the glide planes. According to Sect. 4 two energetically different HN₃ molecules are



Fig. 13. Proposed structure of the monolayer HN_3 adsorbed on the NaCl(100) surface. Shown are the projections of the NNN chains on the surface. The adsorbate unit cell contains two equivalent HN_3 -dimers (1,3), (2,4) each linked by an H bond donated by molecules 1, 2, resp., (species I). Molecules 3, 4, (species II), being further from the surface, point to molecules 1, 2, resp. The other weaker H bond binds the dimers to each other or/and to Cl⁻ ions. Commensurate $p(2 \times 2)$ -lattice. 2D space group pg.

connected by a hydrogen bond. The other weaker H bond is directed to the other dimer or/and to one of the two adjacent Cl⁻ atoms. With respect to the large distance *d* of the two species the structure rather corresponds to a bilayer than to an ordinary monolayer. The obtained vibrational polarizabilities are large compared to the measured gas phase value ($\alpha_{vx} \ge 0.06 \text{ Å}^3$) even if we assume an error of about 0.1 Å³. An enlargement of vibrational polarizabilities has been observed in other adsorption systems as well, e.g. CH₃F-NaCl(100). It might be caused by the strong interaction of the adsorbed HN₃-molecules with each other and with the NaCl substrate as it is expressed by the quite large value of the adsorption enthalpy of about -43 kJ/mol. An influence of the hydrogen bonds is imaginable, too.

As we mentioned above there are two broad absorption bands in the spectral region of the H–N stretching vibration (separated by about 40 cm^{-1}) corresponding to two kinds of hydrogen bonds in the adsorbate. The different strength of these hydrogen bonds might be one reason for the difference between the two vibrational polarizabilities. Moreover, we suppose that the species with the larger polarizability is closer to the surface than



Fig. 14. Calculated spectra of the monolayer $H^{14}N_3$ adsorbed on NaCl(100) in the range of the v_2 mode at *p*- and *s*-polarization (angle of incidence 50°) as a function of the distance d between the energetically inequivalent $H^{14}N_3$ species I and II in the direction normal to the surface. The optimized *d*-value is -3 Å. Dynamic vibrational coupling not only between energetically equivalent but also between energetically inequivalent molecules is concluded.

the other. Further investigations are necessary to explain the observed effects accurately.

In order to analyze the effects of the variation of the distance *d* of the molecular species on the IR spectra and the vibrational coupling we carried out several calculations which are described in the following. An optimization procedure performed assuming a distance d = 0 Å has yielded the pair of spectra in Fig. 12 which is marked with 'pg/d = 0 Å'. The correspondence to the experimental spectra is fair but less than for the pair of spectra 'pg' discussed above. Therefore the distance of the two species should differ from d = 0 Å. In Fig. 14 it is shown that the value of *d* is significant for the appearance of the spectra and the extend of the vibrational coupling between the different molecular species. The *p*- and *s*-polarized spectra have been calculated as a function of *d* with the other simulation parameters remaining constant. For d > 7 Å the interactions between the different species are negligible because the spectra do not change any more. For *d*-values near 0 Å however, peak shifts



Fig. 15. Analysis of the dynamic vibrational coupling between the species I and II in the monolayer of $H^{14}N_3$ -adsorbed on NaCl(100) (*pg* symmetry) by separating their polarized IR-absorptions for the optimized *d* value (*A*) and for infinite distance (*B*).

up to 10 cm^{-1} occur. Nevertheless, the *d*-value determined for the optimized spectra seems to be too large considering the density of condensed hydrogen azide and the estimated coverage in the saturation phase of HN₃-NaCl(100). In Fig. 15 the vibrational coupling between the different species is analyzed by separating their absorptions in case of the optimized value *d* and in case of infinite distance, respectively. The upper spectra (*A*) which correspond to the pair of spectra '*pg*' in Fig. 12 and the pair of spectra '*d* = -3 Å' in Fig. 14, respectively, prove that there is a coupling between energetically inequivalent species causing absorptions at all the positions of the bands in the measured spectra. The 1st pair of HN₃ molecules (species II) e.g. causes a diminution of the absorption at 2149.2 cm⁻¹ and a slight amplification of the absorption at 2162.8 cm⁻¹.

In contrast the molecules of the 2^{nd} pair (species I) cause a distinct amplification of the absorption at 2154.0 cm⁻¹ and the small absorption at 2162.8 cm⁻¹ observed with *s*-polarized light.

In case of infinite distance between the molecular species perpendicular to the surface (*B*) we observe the expected superposition of two independent Davydov dublets where the absorption at 2162.8 cm⁻¹ cannot be seen with *s*-polarized light because of the anti-parallel orientation of the molecules of species II and the resulting dipole moment perpendicular to the surface. Taking into account these considerations the large deviation of the optimized molecular angles ϑ and φ from the values derived from measured A_s/A_p ratios can be understood.

8. Conclusions

It has been shown that hydrogen azide adsorbs molecularly on the NaCl(100) single crystal surface and generates a well-defined and highly ordered adsorbate giving sharp IR-absorptions. To explain the quartet observed in the spectral region of the asymmetric (NNN) stretching mode v_2 isotopic mixture experiments were performed. These experiments gave evidence of a correlation field with long range dynamic dipole-dipole coupling. There are two energetically different species (I and II) of HN₃ molecules within the adsorbate unit cell. Analyzing the polarization dependence of the IR-spectra quantitatively, we were able to estimate molecular tilt angles of the two species (I and II) and intermolecular angles between the energetically equivalent but translationally inequivalent molecules (M1 and M2) assuming that there is no dynamic coupling between species I and II. Spectra simulations, however, have shown that there is indeed a dynamic coupling. Therefore, the results from the quantitative analysis of the IR-spectra have to be treated with some caution. The molecular parameters derived from IR-spectra are listed in Table 1. With respect to the tilt angle of species II we cannot distinguish between the values $\vartheta = 25^{\circ}$ and $\vartheta = 180^{\circ} - 25^{\circ}$. Also we are not able to determine the exact location of the molecules with respect to the substrate, only their location in the adsorbate unit cell. However, the translational geometry has been obtained by means of LEED-measurements showing a $p(2 \times 2)$ superstructure pattern of the saturation phase of HN₃ on NaCl(100). The combination of IR- and LEED-results led to three possible space groups (pg, pm, and pmg) for the adsorbate structure. Based on these experimental data spectra simulations have been performed which have yielded further information about parameters of the adsorbate listed in Table 1. Remarkable is the agreement of the v_1 and v_2 frequencies between the N_2 matrix isolated dimer and the monolayer on NaCl(100), leading to the dimer structure of the monolayer and the assignment of species I as the H bond donor and species II as the H bond acceptor in the dimer on the NaCl(100) surface. Combining the results we propose the following adsorbate structure.

	Species I				Species II				
	tilt angle	tilt inter- ngle molecular angle		Location $x, y[a_0]$		inter- molecular angle	Location $x, y[a_0]$		space group
	ϑ	arphi	M1	M2	θ	arphi	M1	M2	2D
exp.	0° to 10°	50°	_	_	25°	180°	-	-	pg, pm, pmg
sim.	0° assumed	72°	0.91, 0.18	0.41, 0.82	45°	180° assumed	0.25, 0.36	0.75, 0.64	pg

Table 1. Structural data of the monolayer HN₃ adsorbed on NaCl(100). Tilt angles ϑ with respect to the NaCl(100) surface, intermolecular angles φ between energetically equivalent molecules M₁, M₂ and location of the four HN₃ molecules within the adsorbate unit cell obtained from quantitative IR-spectra analysis (exp.) and spectra simulations (sim.).

There is a monolayer forming a commensurate lattice with the translational symmetry $p(2 \times 2)$. Four HN₃ molecules make up the 2D unit cell. Its 2D space group is pg. The molecules are grouped into two energetically different pairs I and II having different orientations and different distances from the surface, the difference being ≤ 3 Å. The molecules of species I lie flat on the surface with an intermolecular angle of 50°, those of species II are tilted, the tilt angle to the surface is 25°, and aligned anti-parallel. The dynamic dipoles of the molecules including those of the energetically different molecules couple to build up collective vibrations. According to the simulation of their spectra the molecules form zigzag chains parallel to the glide planes pg shown in Fig. 13. Two energetically inequivalent molecules are linked by a hydrogen bond forming a dimer, the NH donor being the molecule of species II is directed to the adjacent dimer or/and to a Cl⁻ ion.

Further experimental investigations will provide additional information. Thus, IR-investigations of the temperature dependence of the adsorbate might reveal effects on the hydrogen bonding and therefore might help to clarify the role of this bond within the adsorbate structure. Moreover, a closer inspection of the other fundamentals ($v_3 - v_6$) in particular of the NH mode v_1 will be fruitful for a more refined understanding of the adsorbate structure.

Acknowledgement

The work was performed in the 'DFG-Forschergruppe Adsorbatwechselwirkungen an Ionenkristallen und Metallen'. The support by Deutsche Forschungsgemeinschaft (DFG), Kali und Salz GmbH, Fonds der Chemischen Industrie and Land Niedersachsen is gratefully acknowledged. We thank Prof. H. Willner, Universität Duisburg, for preparing the HN₃-gas used in our experiments and Prof. H. Weiss, Universität Magdeburg, for stimulating discussions.

References

- 1. H.-J. Freund and E. Umbach, eds., Adsorption on Ordered Surfaces of Ionic Solids and Thin Films, Springer-Verlag, Berlin (1993).
- 2. W. Ho, in: Advanced Series in Physical Chemistry, 5(2) (1995) 1047.
- 3. G. Ertl, Ber. Bunsen-Ges. Phys. Chem. 99 (1995) 1282.
- 4. X. L. Zhou, X.-Y. Zhu and J. M. White, Surf. Sci. Rep. 13 (1991) 73.
- 5. Y. J. Chabal, Surf. Sci. Rep. 8 (1988) 211.
- 6. T. J. Chuang, Surf. Sci. Rep. 3 (1983) 1.
- 7. L. W. Bruch, M. W. Cole and E. Zaremba, *Physical Adsorption: Forces and Phenomena*, Clarendon Press, Oxford (1997).
- 8. S. S. Sung and P. C. Jordan, J. Chem. Phys. 85 (1986) 4045.
- 9. S. N. Lin and P. C. Jordan, J. Chem. Phys. 89 (1988) 7492.
- 10. D. Hollenbach and E. E. Salpeter, Astrophys. J. 163 (1971) 155.
- 11. R. Vogt and B. J. Finlayson-Pitts, J. Phys. Chem. 99 (1995) 17269.
- N. Jockwer, in Scientific Basis for Nuclear Waste Management, Plenum, New York, Vol. 3 (1981).
- 13. N. Jockwer and S. Gross, Mater. Res. Soc. Symp. Proceed. 50 (1985) 587.
- 14. A. Singewald und G. Fricke, Chem. Ing. Techn. 55 (1983) 39.
- J. Heidberg, Glückauf 135 (1999) Nr. 7/8, 533 mit Kali und Steinsalz 12 (1999) Nr. 10.
- J. Heidberg, H. Stein, A. Nestmann, E. Hoefs and I. Hussla, in *Laser-Solid Inter*actions and Laser Processing, S. D. Ferris, H. J. Leamy and J. M. Poate, eds., Am. Inst. Phys. Conf. Proc. 50 (1979) 49.
- 17. J. Heidberg, H. Stein, E. Riehl and A. Nestmann, Z. Phys. Chem. N. F. **121** (1980) 145.
- 18. T. J. Chuang, J. Chem Phys. 76 (1982) 3828.
- 19. G. P. Brivio and T. B. Grimley, Surf. Sci. Rep. 17 (1993) 1.
- E. B. D. Bourdon, J. P. Cowin, I. Harrison, J. C. Polanyi, J. Segner, C. D. Stanners and P. A. Young, J. Phys. Chem. 88 (1984) 6100.
- 21. I. Harrison, J. C. Polanyi and P. A. Young, J. Chem. Phys. 89 (1988) 1498.
- 22. J. C. Polanyi and Y. Zeiri, in: Advanced Series in Physical Chemistry 5(2) (1995) 1241a.
- 23. H. Okabe, J. Chem. Phys. 49 (1968) 2726.
- 24. M. Hawley, A. P. Baronavski and H. H. Nelson, J. Chem. Phys. 99 (1993) 2638.
- 25. W. Hack and Th. Mill, J. Mol. Spectrosc. **144** (1990) 358; J. Chem. Phys. **97** (1993) 5599.
- K. H. Gericke, M. Lock, R. Fasold and F. J. Comes, J. Chem. Phys. 96 (1992) 422;
 M. Lock, K. H. Gericke and F. J. Comes, Chem. Phys. 213 (1996) 385.
- D. E. Milligan, M.-E. Jacox, S. W. Charles and G. C. Pimentel, J. Chem. Phys. 37 (1962) 2302; D. E. Milligan and M.-E. Jacox, J. Chem. Phys. 41 (1964) 2838.
 K. Yokoyama, H. Kitaike and T. Fueno, Bull. Chem. Soc. Japan 64 (1991) 1731.
- P. J. Haskins and M. D. Cook, Proc. Symp. Explos. Pyrotech. 13 (1985) II-1;
 M. H. Alexander, T. Hemmer and P. J. Knowles, J. Chem. Phys. 93 (1990) 3307.

- 30. N. B. H. Jonathon, P. J. Knight and A. Morris, Surf. Sci. 27 (1992) L640.
- 31. Y. Bu, J. C. S. Chu and M. C. Lin, Surf. Sci. **264** (1992) L151.
- 32. J. C. S. Chu, Y. Bu and M. C. Lin, Surf. Sci. **284** (1993) 281.
- 33. Y. Bu and M. C. Lin, Surf. Sci. 317 (1994) 152.
- 34. B. D. Thoms and J. N. Russell Jr., Surf. Sci. 337 (1995) L807.
- 35. C. Tindall and J. C. Hemminger, Surf. Sci. 330 (1995) 67.
- S. Briquez, S. Picaud, C. Girardet, P. N. M. Hoang, J. Heidberg and A. Voßberg, J. Chem Phys. 109 (1998) 6435.
- J. Heidberg, A. Voßberg, M. Hustedt, M. Thomas, S. Briquez, S. Picaud and C. Girardet, J. Chem. Phys. 110 (1999) 2566.
- 38. J. P. Toennies, F. Träger and H. Weiss, in preparation.
- 39. M. Grunwald and G. E. Ewing, J. Chem Phys. 109 (1998) 4990.
- J. Heidberg, M. Grunwald, M. Hustedt and F. Traeger, Surf. Sci. 368 (1996) 126; J. Heidberg, E. Kampshoff and M. Suhren, J. Chem. Phys. 95 (1991) 9408; D. Schmicker, J. P. Toennies, R. Vollmer and H. Weiss, J. Chem. Phys. 95 (1991) 9412; S. Picaud, P. N. M. Hoang, C. Girardet, A. Meredith and A. Stone, Surf. Sci. 294 (1993) 149; V. Pouthier and C. Girardet, Phys. Rev. B 60 (1999) 13800.
- H. H. Richardson and G. E. Ewing, J. Electron Spectrosc. Rel. Phenom. 45 (1987) 99; H. H. Richardson and G. E. Ewing J. Phys. Chem. 91 (1987) 5833.
- J. Heidberg, K.-W. Stahmer, H. Stein and H. Weiss, J. Electron Spectrosc. Rel. Phenom. 45 (1987) 87; J. Heidberg, K.-W. Stahmer, H. Stein, H. Weiss and M. Folman, Z. Phys. Chem. N.F. 155 (1987) 223.
- 43. J. Heidberg, E. Kampshoff, H. Stein, H. Weiss and M. Warskulat, Mikrochim. Acta (Wien) II (1988) 105.
- 44. O. Berg and G.E. Ewing, Surf. Sci. 220 (1989) 207.
- J. Heidberg, E. Kampshoff, O. Schönekäs, H. Stein and H. Weiss, Ber. Bunsenges. Phys. Chem. 94 (1990) 112 and 118; J. Heidberg, E. Kampshoff, R. Kühnemuth and O. Schönekäs, Surf. Sci. 267/270 (1992) 120.
- J. Heidberg, E. Kampshoff, R. Kühnemuth, O. Schönekäs, G. Lange, D. Schmicker, J. P. Toennies, R. Vollmer and H. Weiss, J. Electron Spectrosc. Relat. Phenom. 64/65 (1993) 341.
- S. Picaud, S. Briquez, A. Lakhlifi and C. Girardet, J. Chem. Phys. **102** (1995) 7229.
 J. Heidberg, M. Hustedt, E. Kampshoff and V. M. Rozenbaum, Surf. Sci. **427–428** (1999) 431.
- 48. J. Heidberg and W. Häser, J. Electron Spectrosc. Rel. Phenom. 54/55 (1990) 971.
- L. W. Bruch, A. Glebov, J. P. Toennies and H. Weiss, J. Chem. Phys. **103** (1995) 5109; S. Fölsch and M. Henzler, Surf. Sci. **247** (1991) 269; S. Fölsch, A. Stock and M. Henzler, Surf. Sci. **264** (1992) 65.
- B. Ahlswede and K. Jug, Surf. Sci. 439 (1999) 86; K. Jug and G. Geudtner, Surf. Sci. 371 (1997) 95.
- 51. M. C. Foster and G. E. Ewing, J. Chem. Phys. **112** (2000) 6817; O. Engkvist and A. Stone, J. Chem. Phys. **112** (2000) 6827.
- 52. H. Weiss, Surf. Sci. 331-333 (1995) 1453.
- 53. J. Dohrmann, A. Glebov, J. P. Toennies and H. Weiss, Surf. Sci. 368 (1996) 118.
- 54. J. Heidberg, M. Kandel, D. Meine and U. Wildt, Surf. Sci. 331-333 (1995) 1467.
- 55. R. Gerlach, A. Glebov, G. Lange, J. P. Toennies and H. Weiss, Surf. Sci. **331–333** (1995) 1490; V. Panella, J. Suzanne, P. N. M. Hoang and C. Girardet, J. Phys. I (France) **4** (1994) 905.
- 56. J. Heidberg and B. Redlich, Surf. Sci. 368 (1996) 140.
- 57. J. Heidberg, B. Redlich and D. Wetter, Ber. Bunsen-Ges. Phys. Chem. 99 (1995) 1333.

- S. Picaud and C. Girardet, Chem. Phys. Lett. 209 (1993) 340; L. Giordano, J. Goniakowski and J. Suzanne, Phys. Rev. Lett. 81 (1998) 1271.
- D. Ferry, A. Glebov, V. Senz, J. Suzanne, J. P. Toennies and H. Weiss, J. Chem. Phys. 105 (1996) 1697; Surf. Sci. 377–379 (1997) 634.
- 60. A. Crossley and D. A. King, Surf. Sci. 68 (1977) 528.
- 61. G. E. Ewing, Springer Ser. Surf. Sci. 33 (1993) 57.
- M. Henzler, Appl. Surf. Sci. 11–12 (1982) 450; M. Henzler, Appl. Phys. A 34 (1984) 205.
- H. Weiss, Surf. Sci. 331–333 (1995) 1453; J. Heidberg, D. Meine and R. Redlich, J. Electron Spectrosc. Relat. Phenom. 64/65 (1993) 599.
- 64. R. Hammaker, S. Francis and R. Eischens, Spectrochim. Acta 21 (1965) 1295.
- 65. G. D. Mahan and A. A. Lucas, J. Chem. Phys. 68 (1978) 1344.
- 66. B. N. J. Persson and R. Ryberg, Phys. Rev. B 24 (1981) 6954.
- 67. J. Heidberg, M. Hustedt, J. Oppermann and P. Paszkiewicz, Surf. Sci. 352–354 (1996) 447.
- 68. A. S.-C. Cheung and A. J. Merer, J. Mol. Spectrosc. 127 (1988) 509.
- 69. J. Bendtsen and G. Guelachevili, J. Mol. Spectrosc. 165 (1994) 159.
- 70. J. Bendtsen and F. M. Nicholaisen, J. Mol. Spectrosc. 152 (1992) 101.
- H. J. Kreuzer and S. H. Payne, in: *Dynamics of Gas-Surface Interactions*, The Royal Soc. of Chemistry, London (1991).
- E. P. Palik, ed., Handbook of Optical Constants of Solids, Academic Press Inc. London (1985).
- Gmelin, Handbook of Inorganic and Organometallic Chemistry, 8th ed. N, Supplement Vol. B2, Springer-Verlag, Berlin (1993).
- 74. G. C. Pimentel, S. W. Charles and K. Rosengren, J. Chem. Phys. 44 (1966) 3029.
- 75. T. H. Lee, R. J. Colton, M. G. White and J. W. Rabalais, J. Am. Chem. Soc. 97 (1975) 4845.
- 76. M. Born and E. Wolf, Principles of Optics, Pergamon Press, 4th ed. (1970).
- 77. Gmelin, Handbuch der anorganischen Chemie, Kohlenstoff, Teil C, 8. Aufl., Springer Verlag, Berlin (1974).