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Spectroscopic Investigation of Nitric Acid Monohydrate

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Abstract

Vibrational spectroscopy, X-ray diffraction, and electron microscopy have been applied to investigate the crystallization of concentrated amorphous nitric acid ($0.5 \leq x \leq 0.95$). Crystalline nitric acid monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$) is the major hydrate phase detected together with traces of metastable nitric acid dihydrate ($\text{HNO}_3 \cdot 2\text{H}_2\text{O}$) and pure crystalline nitric acid. Nitric acid tetratohydrate ($4\text{HNO}_3 \cdot \text{H}_2\text{O}$) was not achievable. The diffraction data show [nitric acid monohydrate](#) as a highly symmetrical structure, which bestows clearly laid out infrared, Raman and inelastic neutron scattering spectra. The low frequency region is still a matter of discussion since experiment and theory are not in accordance. The microscopic picture underlines the model character of [nitric acid monohydrate](#), since the crystalline particles **adopt a spherical shape, on various agglomeration stages**, which minimizes the interference of scattering on the spectroscopic data.

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Introduction

Nitric acid monohydrate (NAM) has been a subject of research for many different reasons over the years. The first publications concerning NAM were written in 1951 by Luzzati who solved the structure of solid NAM by single-crystal X-ray diffraction (XRD).¹ At [that](#) time, the interest was purely academic and the structures of several acids and their hydrates were solved in a similar way. In 1953 Bethell and Sheppard monitored solid and liquid NAM by IR-spectroscopy.² 15 years later, Janik *et al.* published the first inelastic neutron scattering (INS) experiments on solid NAM and other similar hydrates.^{3,4} They compared their results with existing IR and Raman data. A particular focus was on the low-frequency region. In 1974, Dawber carried out vapour pressure experiments with liquid HNO₃ in the concentration region of NAM, in order to prove the stability of H₃O⁺ and NO₃⁻ ions.⁵ Delaplane *et al.* studied the hydrogen bonds of these NAM constituents using XRD and *ab initio* calculations.⁶ A subsequent paper of Janik *et al.* appeared in 1978, observing also the INS spectra of amorphous NAM and its crystallization changes.⁷ For a closer inspection of the amorphous state, in 1979 Herzog-Cance *et al.* analyzed the glass form of NAM as well as its changes during crystallization using fast Raman and wide-line NMR spectroscopy.⁸

In the early 1980s a decrease of the earth ozone layer was predicted and in 1985 a seasonal ozone depletion in the lower polar stratosphere was observed.^{9,10} In the following years much research was focused on polar stratospheric clouds (PSCs), which play a central role in heterogeneous stratospheric chemistry. Thus, the micro-physical mechanisms of PSC formation became an important issue. Nitric acid hydrates (NAX) were found to be the major constituents of PSCs.¹¹ These findings prompted the gathering of abundant information about the NAX species, including NAM. In this context, Hanson and Mauersberger presented their study of NAM,¹² in which they also measured the vapour pressure over nitric acid mono- and trihydrate. Over the years several groups published infrared and Raman data of NAX comparing the features of the mono-, di- and trihydrate during different annealing procedures.¹³⁻¹⁹ This information was complemented by cluster experiments, kinetic measurements, *ab initio* calculations, and XRD studies.²⁰⁻²⁶ Particularly for the purposes of heterogeneous chemistry, surface spectra of nitric acid hydrates were recorded using diffuse reflectance spectroscopy (DRIFTS), sum frequency

generation (SFG), and grazing-angle reflection absorption infrared spectroscopy (RAIRS).^{22,27-32} These surface investigations showed molecular HNO₃ to be present on the surface of NAM films. For comparison with field measurements the optical constants of nitric acid hydrates were determined.³³

Today it is generally accepted that NAM has no real relevance in the micro-physics of PSCs because of the moderate concentration of nitric acid found at this altitude.

However, the research on NAM carried on for another reason. Theoretical chemists discovered that NAM is a good model substance because it is simpler to calculate than any other hydrate and there already exists abundant information which can be used to test these calculations. During the last 15 years many investigations have been carried out to develop improved theoretical models.^{21,22,34-39} Only recently the X-ray diffraction data have been re-investigated by Lebrun *et al.*⁴⁰ improving the known structure and Walker *et al.*³⁹ have determined the behaviour of NAM up to a pressure of 43 kbar where three different structural phases have been identified.

This paper aims to provide a more comprehensive picture of the structure and spectroscopic properties of NAM. To this end, we present new morphological information from environmental scanning electron microscopy (ESEM) and X-ray diffraction measurements, together with improved INS spectra. In addition, new IR and Raman data, with their spectroscopic analysis, are also given. The article is structured as follows. First, the experimental details of all techniques employed, are described. Next, the results attained by each technique are presented and discussed. The conclusions are outlined in a final section.

In the present paper, new spectroscopic data (FTIR, Raman and INS) and high level quantum chemical calculations are collected. These data are additionally correlated with morphological information from environmental scanning electron microscopy (ESEM).

Experimental

Specific sample preparation methods of NAM depended on the experimental analysis tool to be used. But all ways of preparation were based on concentrated solutions of HNO₃ in H₂O. These solutions were quenched by different methods always with the aim to produce an amorphous sample, which was consequently crystallized in the course of an annealing program which included the following steps:

(I) the amorphous sample was heated (5 K min^{-1}) to a temperature above the glass transition point,

(II) [the sample was kept at the constant temperature of interest until repeated short-term measurements](#), ~~revealed~~ no further changes,

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(III) the sample was cooled back to a temperature below [the glass transition point](#) (125 K) and a long-term measurement [was started](#).

Structural changes in the course of the subsequent thermal treatment were observed by X-ray diffraction, FTIR, Raman and INS spectroscopy. Additionally, environmental scanning electron microscopy was applied to a NAM sample to gain information about its morphology.

The set up for the XRD measurements was the same as that described in ref. 23 and 41 and therefore, it will only be discussed in brief here. It consists of three parts: an aerosol chamber, a sample compartment, and a high vacuum (HV) cryostat. To form the aerosol a Meinhardt[®] nebulizer (TR-50A1) was used to disperse the nitric acid solution. A Teflon slide separates the sample compartment from the high vacuum part with the colder surfaces of the cryostat. Thus, the sample may be kept under its own vapour pressure without any sample transfer to the cold cryostat surfaces. The sample support (gold plated aluminium) is mounted at the cold end of a helium closed-cycle cryostat (RGD 210 Leybold, Germany) which is located in the centre of a two cycle goniometer in Bragg-Brentano θ - θ -geometry (3000TT Seifert, Germany). Ni-filtered copper radiation ($\lambda_1(\text{Cu-K}\alpha_1)$: $1.54051 \text{ \AA}$; $\lambda_2(\text{Cu-K}\alpha_2)$: $1.54433 \text{ \AA}$) illuminates the sample through an aperture closed with a metalized Mylar foil of $40 \text{ }\mu\text{m}$ thickness. The scattered rays were collected by a scintillation counter.

The FTIR set-up was specially designed to protect its sensitive optical components in the course of quenching the aggressive mixtures. A detailed description of the apparatus can be found in the work of Tizek et al.⁴¹ The HV-cryostat chamber can be separated by a gate valve into a measurement chamber inside and a sampling compartment outside the spectrometer. An edge welded bellows with a jounce travel of 200 mm permits the sample support to be moved from one position to the other without any deterioration of the vacuum conditions. Spectra were recorded by co-addition of 10 scans at a resolution of 4 cm^{-1} with a Bruker 113v spectrometer (Karlsruhe/Germany). The IR-beam was focused on the gold plated sample support where the sample was analyzed in double transmission. Cooling was performed via dry air which was precooled to 80 K by heat exchange with liquid nitrogen. The

coolant flowed into the sample carrier in the inner one of two concentric tubes and left the cryostat via the outer one. Thus a minimum temperature of less than 90 K is achieved. A temperature sensor (thermocouple) is located in an orifice directly below the carrier surface. Its accuracy could be determined by analyzing the vapor pressure of water and the α -/ β -transition of cyclohexane and it amounted to ± 1 K. FTIR measurements require only a few seconds' time and spectra could be taken throughout the thermal treatment of the sample.

The preparation techniques for ESEM differ somewhat from the others. While in the case of XRD and FTIR an aerosol was deposited, for ESEM a droplet of approximately 4 μ l was quenched in a liquid nitrogen bath. To analyze the NAM sample the method of freeze fracturing proved to be very useful. A sample carrier with a hole was filled with the liquid sample thus producing a drop that projected above the hole. Then the sample carrier with the sample was quenched in liquid nitrogen and transferred to the preparation chamber of the ESEM. In the preparation chamber all parts were cooled with liquid nitrogen to a temperature of about 110 to 125 K. The portion of the sample drop which lay above the sample carrier was broken away by a cold edge of a weld manipulator. The so-gained surface is clean and virgin and enables a very good analysis of the sample. Environmental scanning electron microscopy (ESEM) can be operated at higher pressures than traditional SEM. The NAM sample was observed under the pressure of an imaging gas (N_2) thus preventing the sample from evaporating. The measurements were done on a FEI Quanta 200 3D DBFIB at the University Service Centre for Transmission Electron Microscopy (USTEM) at the Vienna University of Technology. The annealing process was initiated in this case by stepwise heating the cryo-stage in the ESEM to the desired temperature. This procedure allows taking pictures while manipulating the temperature of the sample.

The production of samples for Raman spectroscopy was quite simple. For this purpose small glass capillaries (outer diameter 2 mm, wall thickness 0.5 mm, length 15 mm) were filled with 4 μ l nitric acid solution (50 mol%). After the capillary was filled it was dipped into a liquid nitrogen bath where the sample froze to give an amorphous solid. This worked very well and was reproducible due to the very efficient heat exchange. The capillary containing the sample was then transferred into a cryostat where a temperature of 140 K was maintained by a cold nitrogen gas stream. The detailed description of this cryostat can be found elsewhere.⁴² The annealing could be done with a heating rate of approximately 5 K min⁻¹. The spectra were recorded using a Dilor

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RTI30 spectrometer equipped with an argon ion laser (514.5nm). The laser was guided through the double walled glass cryostat onto the sample capillary and the scattered light was collected perpendicular to the incident laser.

The INS measurements were carried out using TOSCA⁴³ spectrometer at the ISIS Facility.⁴⁴ TOSCA offers high resolution, $\sim 1.25\% \Delta E/E$ between 16 and 4000 cm^{-1} . The cryostat on TOSCA consists of a single stage closed cycle refrigerator (CCR, [Leybold](#)) that cools an outer radiation shield to ~ 45 K and two dual stage 4 K CCRs (Sumitomo) that cool a central chimney, at the bottom of which the sample is mounted on the end of a special pole, a centrestick. (The neutron beam passes through the lower part of a cryostat.) The sample is cooled by [convection](#) across a low pressure, 20 mbar, of helium exchange gas. To change sample, the chimney is filled with helium gas to atmospheric pressure, the centrestick withdrawn and exchanged for another with the next sample attached. The chimney is then evacuated to its operational pressure and the sample allowed to cool. The sample changeover can easily be accomplished in less than half-an-hour and the sample cools to base temperature (~ 12 K) in about two hours. For the sample preparation small droplets of about 4 μl were quenched one after another directly in a liquid nitrogen bath. After that they were transferred onto the sample carrier still under liquid nitrogen. During this procedure the uttermost care was needed not to touch the sample with any parts that had not been cooled to liquid nitrogen temperature to avoid partial crystallization of the amorphous sample. The sample carrier was then transferred quickly out of the nitrogen bath into the cryostat of the TOSCA apparatus which had a temperature of approximately 20 K. Then the analysis was started. A spectrum at 20 K was first recorded to ensure the amorphicity of the sample. In the annealing procedure the NAM sample was heated to 180 K, cooled down, and finally the spectrum of the crystallized phase was recorded.

Results

[XRD data](#)

Nitric acid monohydrate crystallizes in the orthorhombic space group $P2_1cn$ with cell parameters $a=6.317(3)$ Å, $b=8.723(4)$ Å and $c=5.477$ Å (see [Figure 1](#)).⁴⁰ The crystallographic data [were](#) used for calculating the powder diffractogram, shown at top of Fig. [2a](#) as a bar diagram, in comparison with an experimental diffractogram of the 1:1 stoichiometry mixture. There is ample accordance, not only in signal positions but also in the relation of reflections' intensities [\(not evident in the bar](#)

[diagram shown here](#)). Disturbing influences like texture effects appear only to a very minor extent and do not affect the present analysis, which makes further refinement unnecessary.

Figure 1

The diffractograms in Figure [2a](#) exhibit a clearly observable phase transition from amorphous to crystalline NAM starting at about 154 K, which is 4 K above the glass transition point of the sample.⁴⁵ In general, the diffractogram of an amorphous sample is unstructured and exhibits a broad intensity distribution about a wide angle range. [In addition to the signal from the sample](#), there is also a signal from the cryostat itself, which results from the windows material and the sample carrier. During crystallization the respective reflections grow upon this background.

[FTIR data](#)

Whereas X-ray diffraction [data](#) supply the fundamental information of a phase transition, i.e. a change in the long-range order of the sample structure, vibrational spectroscopy can furnish information on the short-range order structural changes occurring during this phase transition. In Figure [2b](#) there are three main frequency regions where changes become most obvious:

- Between 3300 and 3000 cm^{-1} the typical absorptions of the OH-stretching vibrations of water disappear during crystallization.
- Conversely, strong bands at 2644 and 2226 cm^{-1} grow in the same process. These bands can be associated with ν_1 and ν_3 of H_3O^+ whereas the emerging bands at 1663 cm^{-1} and 1116 cm^{-1} are assigned to ν_4 and ν_2 of the same cation, respectively.³⁶
- A strong absorption at 1238 cm^{-1} can be assigned to the [anti](#)symmetric stretching band of NO_3^- . The symmetric stretching band $\nu_1(\text{NO}_3^-)$ is infrared inactive. It is not observed at 1050 cm^{-1} , [but](#) it does appear in the spectra of other nitric acid hydrates, sometimes as a split feature, revealing an asymmetric environment of the nitrate group.

Thus, the infrared spectrum provides evidence that in the amorphous sample (lowest trace in Fig. [2b](#)), dissociation of the acid is not complete, and the neutral species coexist with a partial concentration of the ions. In addition, trace amounts of N_2O_4 have been trapped and detected (1742 and 1761 cm^{-1}). This dimer is formed due to

the decomposition of nitric acid vapor (the partial pressure of which is ~14 mbar above the solution), and is observed thanks to the strong absorption intensity of these bands in the dimer. After crystallization, nitric acid monohydrate exhibits a complete dissociation into NO_3^- and H_3O^+ as shown in the crystallographic scheme of Figure 1, where no molecular HNO_3 is present. All constituents are dissociation products and all oxygen and hydrogen atoms are connected via hydrogen bonds within each layer. Every oxonium ion is linked to three planar nitrate ions. In this manner, layers of nitrate and oxonium are built up, being interconnected to each other by weak van der Waals forces.

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Figure 2

Higher HNO_3 concentrations, with $0.5 < x < 0.95$, have also been investigated. Pure nitric acid and NAM crystallize according to the respective stoichiometry, as expected from the phase diagram.^{46, 47} Traces of α -NAD (phase I) appear due to the non-equilibrium conditions when crystallizing from the amorphous sample.^{23, 48} With increasing concentration, the point of nitric acid crystallization drops below the of NAM. Figure 3 displays results for a nitric acid concentration of 54 mol%.

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The presence of crystalline nitric acid is confirmed by a XRD reflection at 26.3° (Fig. 3, grey field). During annealing, the pure nitric acid starts to melt at the eutectic temperature of 208 K yielding NAM and the liquid phase (Fig. 3, 210 K, top trace). Finally, it must be stated that no signs have been found for the existence of a tetrahydrate $4\text{HNO}_3 \cdot \text{H}_2\text{O}$ ($x=0.83$) which has been postulated based on differential scanning calorimetry, Raman spectroscopy, and vapour pressure measurements.^{49, 50} In the test described here there are no other important changes besides the disappearance of the nitric acid signal (labeled NA) above the eutectic point at 208 K. The monohydrate melts in accordance to the literature phase diagram at around 235 K.

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Figure 3

Undiluted nitric acid ($x \sim 0.95$) has been investigated as well but could not be frozen out fully amorphously: Several sharp and intense reflections appear on the

unspecific background of the amorphous fraction (diffractogram not shown). The [nitric acid](#) ambient-pressure phase I has been identified unambiguously.⁵¹ Neither from the diffractograms nor from the IR spectra can the ratio between amorphous and crystalline structures be derived. Obviously, pure [nitric acid](#) has a very low glass transition point.⁴⁵ Crystallization of [nitric acid](#) already proceeds below 150 K. Therefore, measurements above 160 K rarely show any differences. Minor parts of the diffractogram show accordance with the diffraction pattern of NAM, the development of which indicates a slight crystalline impurity in the phase composition. The water of the NAM structure originates from the dissociation of HNO₃ into H₂O and NO₂. Traces of N₂O₄ are detectable in the IR spectrum.

INS data

The spectrum labelled with 20 K in [Fig. 4](#) is the first spectrum taken just after the sample was loaded into the cryostat, following the protocol described in the experimental part. At this stage, the sample is [amorphous](#) and has not been annealed yet. The spectrum largely resembles that of strongly disordered water found on metal [oxides](#)⁵²⁻⁵⁵ and is assigned similarly: water translational and librational modes [from 0 to 300 cm⁻¹](#) and [from 300 to 1100 cm⁻¹](#), respectively, and the H–O–H scissors vibration at ~1600 cm⁻¹. The O–H stretching modes are not seen on TOSCA because the momentum transfer, Q (Å), and the energy transfer, E_t (cm⁻¹) are related by $Q^2 \sim E_t/16$ and thus for large energy transfer, Q is also large and all the spectral intensity lies in the phonon wings (combinations of the internal modes and the external density of states), and as a result the high-frequency fundamentals are not observed.⁵⁶ The only evidence for the presence of nitric acid is the peak at ~1430 cm⁻¹ assigned to the N–O–H bend.

As expected from the phase diagram and shown by XRD ([Fig. 2a](#), trace (2)), the amorphous 50 mol% nitric acid solution is fully converted into NAM, the only phase to crystallize, upon annealing to 180 K. Immediately after tempering for 30 minutes, the sample was fast cooled to 20 K. Since the amorphous/crystalline phase transition is irreversible, the measurement could be carried out at 20 K without interference. A spectrum with many intense narrow bands is thus recorded ([Fig. 4](#), trace 2) and the difference to the spectrum of the amorphous phase (trace 1) is striking.

Our high resolution INS spectrum allows resolving broad structures as seen in the previous low resolution INS measurements by Janik *et al.*³. For example, the broad

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feature at 758 cm^{-1} observed by these authors is decomposed into at least six different bands in our work.

The uppermost [calculated](#) spectrum (trace 3) [was](#) generated from a previously reported³⁷ DFT calculation by the program ACLIMAX.⁵⁷ Inspection of the eigenvectors shows that the INS spectrum is dominated by modes involving the H_3O^+ ion and can be divided into [four](#) regions: translational modes [from 0 to 300](#) cm^{-1} , librational modes [from 600 to 900](#) cm^{-1} , H–O–H bending modes [from 900 to 1700](#) cm^{-1} and overtones and combinations at $> 1700\text{ cm}^{-1}$. It can be seen that the H–O–H bending modes are reasonably well described, the librational modes are calculated somewhat higher than observed and the translational modes, shown in more detail in [Fig. 5](#), are poorly represented by the calculation.

The reduced agreement between the observed and calculated INS spectra in the low-frequency region arises from the choice of model employed. The energies and vibrational modes are calculated at the Γ -point (*i.e.* at wavevector $\kappa=0$) in the Brillouin zone, where infrared and Raman modes are allowed. In contrast, INS spectroscopy is sensitive to all wavevectors across the complete Brillouin zone. In cases where there is little or no dispersion in the modes there is usually good agreement between a Γ -point calculation and the observed spectra.⁵⁶ That this is not the case for the present study [but](#) is strong evidence that there is significant dispersion in the modes. Hydrogen-bonded systems are well known to exhibit dispersion and the present example is a textbook case where such effects would need to be considered to accurately model the INS spectrum. Unfortunately, such a calculation is beyond our available resources.

Figure 4

The low-frequency region is enlarged in [Fig. 5](#) where the calculated IR spectrum and the observed INS and Raman spectra (traces 1 to 3 respectively) are shown. The sample for the Raman spectrum was prepared in the way described above (ref. 19). All three spectra seem different at first glance, as corresponding to the diverse techniques used in each case. All vibrations where hydrogen is involved produce a strong signal in the INS spectrum, whereas in the Raman spectrum all vibrations which involve the movement of an oxygen atom are more intense due to the favoured change in polarizability, related to the higher electron density on oxygen

atoms. The spectral features represented in Fig. 5 are listed in Table 1, with previous INS data and a tentative assignment of some modes. Some agreement can be found, especially in band positions, in the two regions alternatively covered by Raman observations and IR predictions. In the Raman and lower frequency part of the INS spectra, the two most prominent features seem correlated, with a small red shift in the Raman. In the higher frequency spectral region of the figure, the peak at $\sim 320 \text{ cm}^{-1}$ is present in both the INS and the predicted IR spectra, whereas the neutron scattering bands in the 200 to 250 cm^{-1} zone seem to be more spread in the calculated infrared trace. Atomic displacements per normal mode derived in the calculations indicate that most of these vibrations can be described as in-phase and out-of-phase twisting of the NO_3^- group and flattening of H_3O^+ .

Figure 5

Table 2 presents a summary of previous and current assignments in the region between 600 and 1700 cm^{-1} , covered by the INS measurements, as shown in Fig. 4. In general terms, there is a reasonably good agreement among all series of IR measurements and with the present INS spectra. The strongest INS bands correspond to vibrations of the oxonium ion: torsion, symmetric bending and asymmetric bending, at $\sim 750 \text{ cm}^{-1}$, 1130 cm^{-1} and 1670 cm^{-1} respectively, whereas the strongest IR bands are those assigned to the asymmetric stretching of the NO_3^- ion, at 1315 cm^{-1} .

Table 1. Low frequency vibrations (in cm⁻¹) of NAM

INS ^a	IR ^b	Raman ^c	INS ^d	Assignment ^e
59		58		
70		75		
90		86		
		101		
124		118	112	
135		129		
154		143		
162			164	
203	195		206	Tz
216				
238	234			
249	268		246	Ty
300	304			
318	320(sh)		321	Tx+Tz
387				
421				

^a INS data from this work, ^b IR calculations by Escibano et al.⁵⁹, ^c Raman data by Grothe et al.¹⁹, ^d INS data from Janik et al.⁴, ^e assignments by Janik et al.⁴

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Table 2: Vibrational spectroscopy data of NAM in the mid-IR region (in cm⁻¹)

INS ^a	IR ^b	IR ^c	IR ^d	IR ^e	Raman ^f	INS ^g	Assignment ^h
603							
673		675	670	680			(H ₃ O ⁺) tors.
	702	700		702			v _L (H ₃ O ⁺)
718	721	723	723	722			v ₄ (NO ₃ ⁻) δ _{as}
	735	737	738	735			v ₄ (NO ₃ ⁻) δ _{as}
750						758	(H ₃ O ⁺)Rz+Ry
770	780			775			
798	814	815	816	813			v ₂ (NO ₃ ⁻) δ _s
877							
926							
969							calc.(NO ₃ ⁻) v ₁
					1044		
					1055		
1103	1102						
1114				1115			v ₂ (H ₃ O ⁺) δ _s
1131	1135	1135	1134				
	1279			1260			v ₃ (NO ₃ ⁻) v _{as}
1314				1316			v ₃ (NO ₃ ⁻) v _{as}
1327							
1402		1386	1361				
1423							
1437							
1459							
1669	1674	1680	1671	1671			v ₄ (H ₃ O ⁺) δ _{as}

^{a)} INS data from this work, ^{b)} IR data by Ritzhaupt and Devlin¹³, ^{c)} IR data by Savoie and Giguere⁵⁶, ^{d)} IR data by Bethell and Sheppard², ^{e)} IR data by Smith et.al.¹⁴, ^{f)} Raman data by Grothe et al.¹⁹, ^{g)} INS data by Janik et al.⁴, ^{h)} the assignments are summarised from the different sources mentioned in the table.

ESEM data

During the laborious preparation of the sample outside and inside the microscope (see experimental section), the sample temperature was scrupulously kept below 125 K, which is 30 K beneath the glass transition point of NAM. Thus, an amorphous state can be guaranteed when comparing with XRD and spectroscopic data. During the annealing the electron beam intensity was reduced in order to avoid damage to the sample or the initiation of an uncontrolled crystallization. Microscope pictures of high resolution were recorded only after re-cooling to T ≤ 125 K.

Figure 6

In Figure 6 the picture (a) shows an unstructured surface, which is in accordance with the assumption of a fully amorphous sample. In the pictures (b-d) the ongoing growth of the crystalline particles can be seen. After 10 minutes small spherical particles (~200 nm in diameter) can be detected (Fig. 6b). Ten minutes later (Fig. 6c), the spheroids have increased their diameter by a factor of 5 (i.e. a growth rate of 80 nm min^{-1}), which corresponds to a volume gain of 125 in 10 minutes. This panel shows a mixture of particles at different stages in their growing process. After a further 10 minutes interval, the spheroids have merged forming a flocced carpet of NAM (Fig. 6d), in which individual spherical particles can still be detected on the surface of the structure.

Conclusions

NAM has been crystallized from various concentrated nitric acid solutions under extremely non-equilibrium conditions. Only one NAM phase (I) has been observed at low temperature and at ambient pressure, the same phase (I) achieved at 11 kbar, as stated in the literature,³⁹ while the two further NAM phases (II, III) are only accessible at much higher pressure (42 and 43 kbar). Clearly, they cannot be generated by any non-equilibrium conditions at ambient pressure. Spectroscopy and diffraction experiments indicate the presence of pure HNO_3 in the amorphous samples, in accordance with previous SFG, DRIFTS, and RAIRS data and theoretical studies.^{60, 61} The reasons for that are, on one hand, demixing according to the phase diagram, and on the other hand, the elevated vapour pressure of HNO_3 above the liquid. Molecular nitric acid is stabilized due to solvation but it tends to decompose into water and NO_2 , which has also been observed by spectroscopic means. The present INS data exhibit a much higher quality and better spectral resolution than the literature data,^{3, 4} and have allowed to resolve some new band positions of water torsions and oxonium hindered rotations.

The ESEM pictures presented here provide unprecedented detail of the structure of NAM, which appears to be formed by spherical crystalline particles in various stages of agglomeration. This conclusion applies to samples grown on a gold support, whereas air-transported particles might be different. However, if we assume a

spherical morphology of the particles then this is a rather ideal case for vibrational spectroscopy, since Mie scattering of aspherical particles would have distorted the transmission spectra particularly in the region of the stretching bands.⁶²

NAM and NAT are the only thermodynamically stable hydrate phases of the nitric acid/water phase diagram. However, from the viewpoint of stratospheric chemistry NAM has only minor relevance because the HNO₃ concentration in atmospheric aerosols at stratospheric altitude does not reach an elevated value. In non-equilibrium processes, NAM could also be formed through the disproportionation of NAD which would produce metastable NAM crystallites.

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Captions to figures:

Fig.1: Projection of the crystal structure of NAM on the [001]-plane. This structure was calculated by refinement of the observed X-ray diffraction result. NAM consists of separated and corrugated two-dimensional layers.⁴⁰

Fig.2 a) (1) X-ray diffractogram of an amorphous sample with $x=0.5$ at $T \leq 125$ K. (2) [X-ray diffractogram of](#) the same sample after annealing to 180K. The bar graph at top shows calculated reflections of NAM. SC indicates reflections of the sample carrier and the window.

Fig.2 b) (1) FTIR-spectrum of amorphous NAM at 125 K. (2) [Spectra of the same sample after crystallization at 180 K, and \(3\) annealed at 200 K, respectively.](#)

Fig.3: X-ray diffractogram of 54 mol% nitric acid at 180 K, 200 K and 210 K. A reflection at 25.5° indicates pure nitric acid and is shaded in grey (and labelled NA). It disappears above the eutectic temperature. A reflection at 15.9° is an impurity of α -NAD and is marked with "D".

Fig.4: INS spectra of NAM evolving from an amorphous phase of 50 mol% nitric acid through annealing. The spectrum (1) shows the amorphous nitric acid ice mixture at 20 K as deposited before annealing. The spectrum (2) is taken after annealing to 180 K. Spectrum (3) is a calculated spectrum for NAM.

Fig.5: Comparison of the low frequency range spectra of NAM by Raman (3) and INS (2), both experimental, and IR, calculated (1).

Fig. 6: ESEM pictures of NAM: (a) amorphous sample at $T \leq 125$ K, (b) crystalline sample at $T=180$ K, after 10 min annealing time, (c) same sample and same conditions but [after](#) 20 min annealing [time](#), (d) as before but [after](#) 30 min annealing time.

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Table 1. Low frequency vibrations (in cm⁻¹) of NAM

INS ^a	IR ^b	Raman ^c	INS ^d	Assignment ^e
59		58		
70		75		
90		86		
		101		
124		118	112	
135		129		
154		143		
162			164	
203	195		206	Tz
216				
238	234			
249	268		246	Ty
300	304			
318	320(sh)		321	Tx+Tz
387				
421				

^a INS data from this work, ^b IR calculations by Escibano et al.⁵⁵, ^c Raman data by Grothe et al.¹⁹, ^d INS data from Janik et al.⁴, ^e assignments by Janik et al.⁴

Table 2: Vibrational spectroscopy data of NAM in the mid-IR region (in cm^{-1})

INS ^a	IR ^b	IR ^c	IR ^d	IR ^e	Raman ^f	INS ^g	Assignment ^h
603							
673		675	670	680			(H ₃ O ⁺) tors.
	702	700		702			ν_L (H ₃ O ⁺)
718	721	723	723	722			ν_4 (NO ₃ ⁻) δ_{as}
	735	737	738	735			ν_4 (NO ₃ ⁻) δ_{as}
750						758	(H ₃ O ⁺)Rz+Ry
770	780			775			
798	814	815	816	813			ν_2 (NO ₃ ⁻) δ_s
877							
926							
969							calc.(NO ₃ ⁻) ν_1
					1044		
					1055		
1103	1102						
1114				1115			ν_2 (H ₃ O ⁺) δ_s
1131	1135	1135	1134				
	1279			1260			ν_3 (NO ₃ ⁻) ν_{as}
1314				1316			ν_3 (NO ₃ ⁻) ν_{as}
1327							
1402		1386	1361				
1423							
1437							
1459							
1669	1674	1680	1671	1671			ν_4 (H ₃ O ⁺) δ_{as}

^{a)} INS data from this work, ^{b)} IR data by Ritzhaupt and Devlin¹³, ^{c)} IR data by Savoie and Giguere⁵⁶, ^{d)} IR data by Bethell and Sheppard², ^{e)} IR data by Smith et.al.¹⁴, ^{f)} Raman data by Grothe et al.¹⁹, ^{g)} INS data by Janik et al.⁴, ^{h)} the assignments are summarised from the different sources mentioned in the table.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6