Metastable Nitric Acid Trihydrate in Ice Clouds

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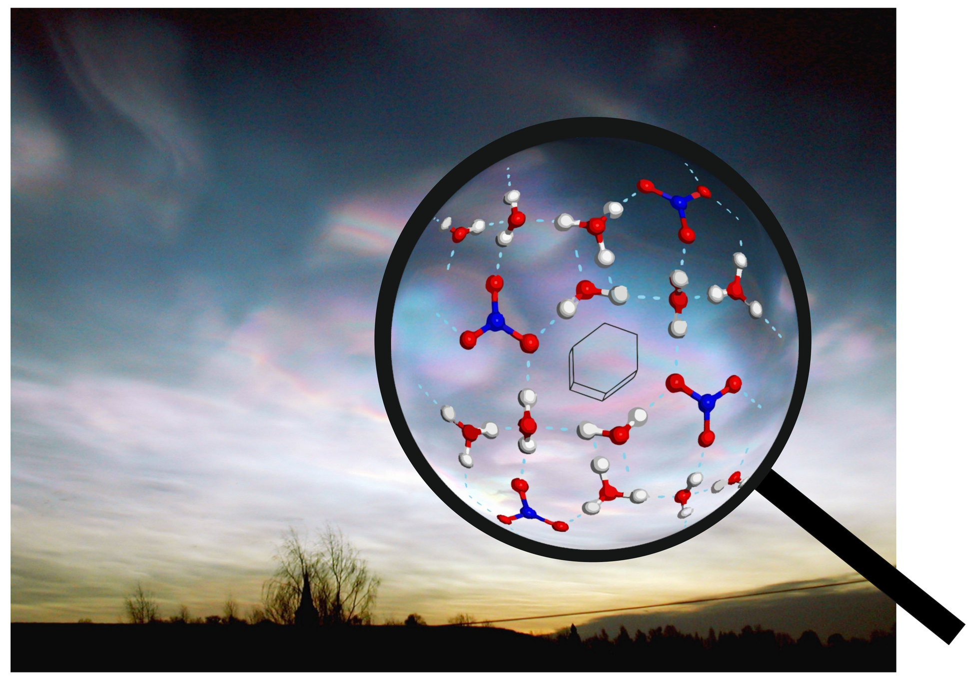
Introduction

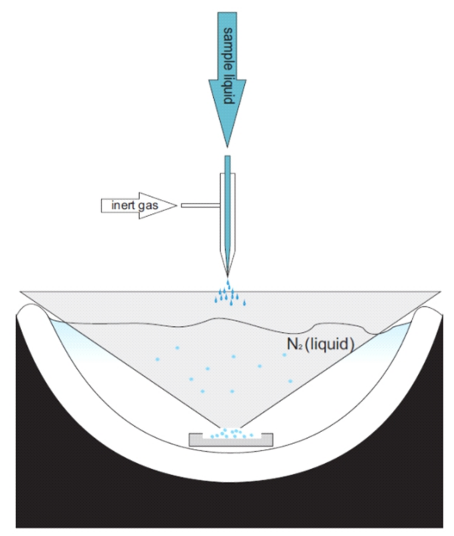
For the Earth's weather and climate system, clouds are of major importance. On one hand they can act as a cooling factor by reflecting parts of the solar radiation and on the other hand they can also cause warming by absorbing solar radiation and by trapping the outgoing infrared radiation. But these effects are not yet so well understood as to enable determinations about the overall radiation balance of the planet [1]. Clouds and aerosol particles are presented as the largest non-anthropogenic uncertainty factor of the radiation balance in the report of the International Panel on Climate Change (IPCC) [2].



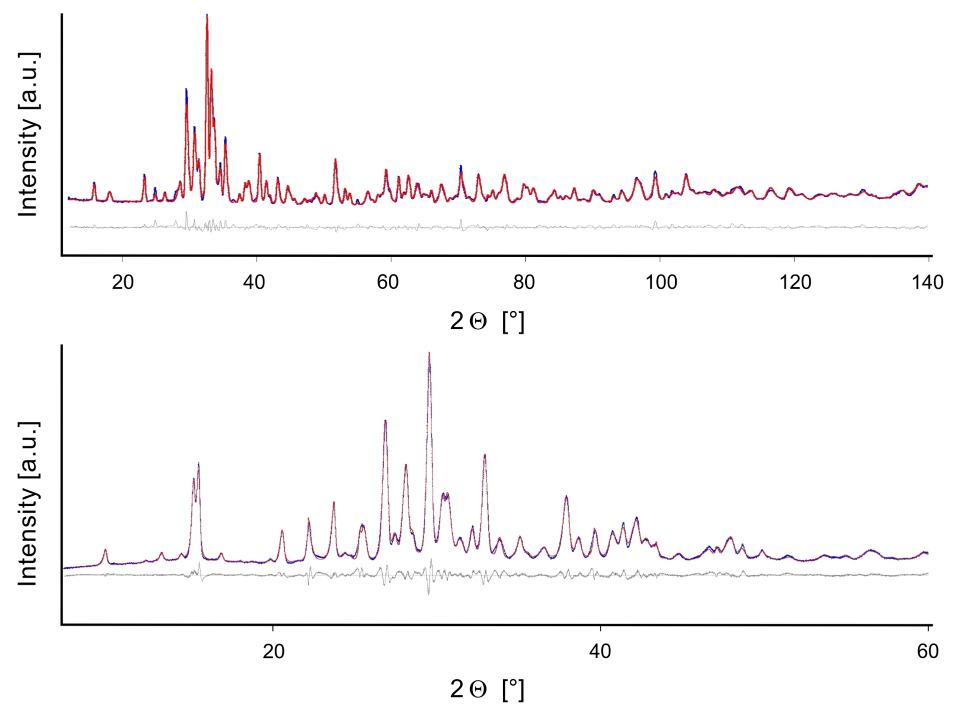
The composition of high altitude ice clouds is still a matter of intense discussion. The constituents in question are ice and nitric acid hydrates. The identification and formation mechanisms, however, are still unknown but are essential to understand atmospheric processing. We found conclusive evidence for a long-predicted phase, which has been named alpha nitric acid trihydrate (alpha-NAT). This phase has been characterized by a combination of X-ray and neutron diffraction experiments allowing a convincing structure solution. Additionally, vibrational spectra (infrared and inelastic neutron scattering) were recorded and compared with theoretical calculations. A strong affinity between water ice and alpha-NAT has been found, which explains the experimental spectra and the phase transition kinetics essential for identification in the atmosphere. On the basis of our results, we propose a new three-step mechanism for NAT-formation in high altitude ice clouds.

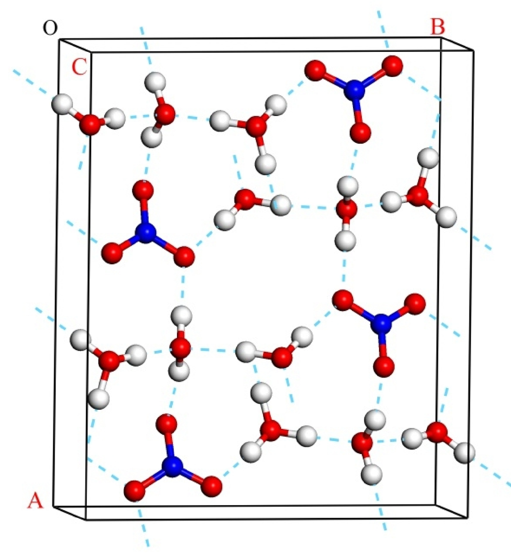
Experiments

Sample production and transport are a very delicate tasks for metastable NAT as the sample is produced in an amorphous state (by dispersing liquid NAT directly into liquid nitrogen) and shall only transition into the metastable phase when already inside a diffractometer. So the sample is always kept in liquid nitrogen. To avoid contamination of the sample, the production procedure was conducted in a purgebox filled with nitrogen



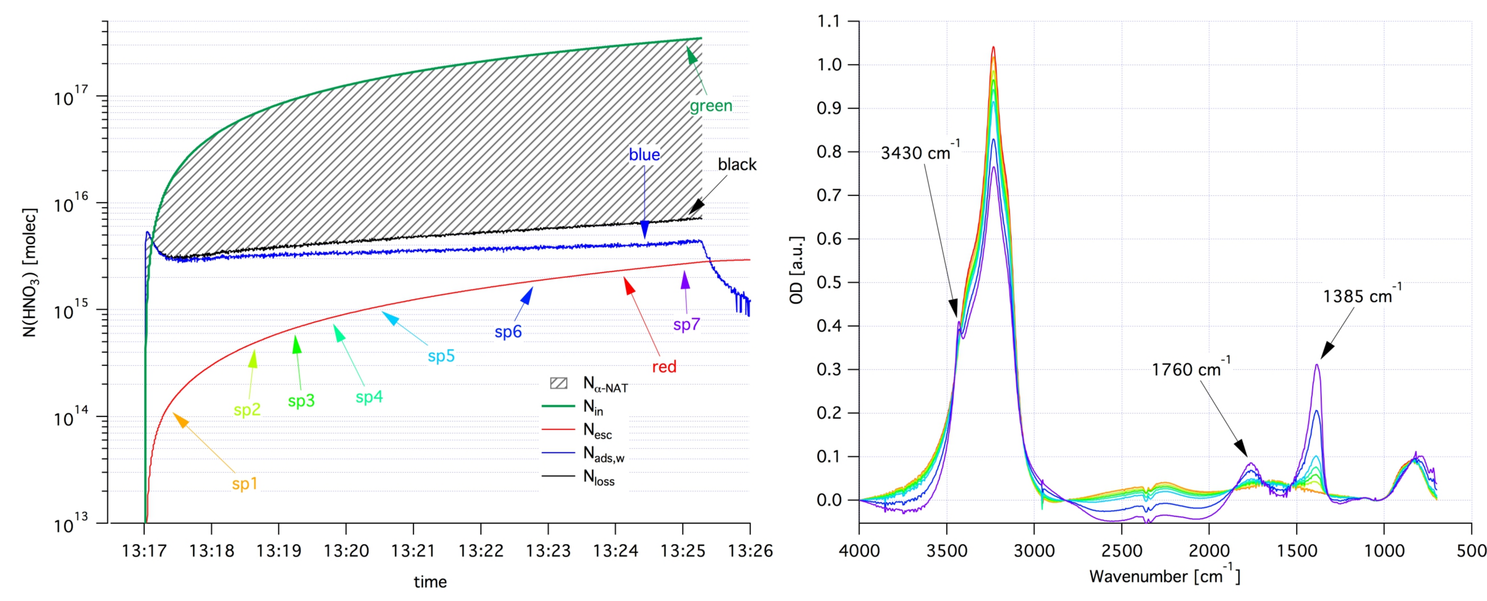
This amorphous sample was transfered to X-ray and neutron diffractometer, where it was annealed to 155 K to recieve metastable alpha NAT.





The Diffractograms show the neutron diffraction pattern of alpha NAT on the top and the X-ray diffraction pattern on the bottom. The shown structure is devised of neutron and x-ray diffraction data. Blue dots - nitrogen; Red dots - oxygen; grey dots - hydrogen.

Now the question arises: why should this complicated to produce phase occur under natural circumstances? Stirred flow reactor studies showed, that when HNO_3 is deposited on an ice film, it is metastable alpha NAT which is formed first and transforms afterwards into beta NAT.



The figures on the top row show HNO_3 deposition onto a pure ice film at 182 K. The right panel shows the temporal evolution of the composite FTIR absorption spectrum starting with pure ice (red trace) and ending with a mixture of alpha-NAT and ice (purple trace). The upper left panel shows cumulative numbers of molecules: green: HNO_3 admitted into SFR (N_{in}), red: HNO_3 lost through effusion out of SFR (N_{esc}), blue: HNO_3 lost to the stainless steel walls of SFR ($N_{ads,w}$), black: total loss of HNO_3 (sum of red and blue, N_{loss}). The total HNO_3 adsorbed on ice corresponds to the hatched area between the green and the black trace ($N_{alpha\text{-}NAT}$). The color-coded labels correspond to the FTIR spectra in the upper right panel.

The conditions in the upper troposphere / lower stratosphere allow for alpha NAT to be formed and we therefore define a 3-step mechanism for NAT formation in high altitudes:
(I) formation of alpha-NAT
(II) spontaneous conversion of alpha- to beta-NAT
(III) subsequent growth of beta-NAT
By solving the structure of one of the early phases of high altitude cloud formation we hope that we can shed light on processes which are still not well understood.

References

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[2] Intergovernmental Panel on Climate Change, Assessment Report “Climate Change 2013: The Physical Science Basis, Summary for Policymakers”, Geneva, 2013; www.ipcc.ch

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