Metastable NAT in Ice Clouds

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Motivation

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]. Polar Strato-spheric Clouds and Cirrus Clouds contain both, pure water ice and phases of nitric acid hydrates. Of

the latter, the thermodynamically stable phases have been intensively investigated in the past (beta-Nitric Acid Trihydrate). As shown by Peter et al. [3] the water activity inside clouds is higher than expected, which might be explained by the presence of metastable phases (e.g. cubic ice). However, also metastable nitric acid hydrates might be important due to the

inherent non-equilibrium freezing conditions in the upper atmosphere. The delta ice theory of Gao *et al.* [4] presents a model approach to solve this problem by involving both metastable ice and NAT as well. So it is of high interest to investigate the metastable phase of NAT.



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Sample Preparation and Measurement

For the metastable NAT phase, alpha NAT, a special preparation method had to be applied. The idea was, that one can reach the metastable phase by coming from the most disordered phase, the amorphous, and slowly heating to the desired temperature. Therefore an amorphous sample had to be produced. This was accomplished by dispersing small droplets of aqueous nitric acid solution directly into liquid nitrogen. A special "prep" box was constructed to purge the surroundings of any water, as this would disturb the measurement, especially if the samples were used for neutron diffraction.







9600 87000 78000

The diffractogram on the upper left shows the alpha NAT phase captured via Xray diffraction at 155 K. The bottom left diffractogram shows the same phase, but as measured by neutron diffraction at 159 K and measured at 4 K. With these two datasets a structure solution was attempted. A schematic view of the production of the amorphous sample can be seen on the bottom.

Alpha NAT Structure



NITROGEN OXYGEN HYDROGEN

The structure of alpha NAT can be seen in the picture top, where Blue represents Nitrogen, Red - Oxygen and Silver - Hydrogen/Deuterium Atoms. It is a monoclinic system with the spacegroup P21/a.

The picture on the left shows the SPODI instrument at the FRM II. The top picture shows the "prep" box, where sample production took place.

The neutron diffraction measurements took place at the FRM II in Munich, at the instrument SPODI. For these measurements special deuterated samples were produced with an emphasis on being water free for getting the best quality diffractograms possible.





Stirred Flow Reactor Studies and Quantum Mechanical Calculations

The figures on the top row show HNO₃ 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: HNO₃ lost through effusion out of SFR (N_{esc}) , blue: HNO₃ lost to the stainless steel walls of SFR (N_{ads.w}), black: total loss of HNO₃ (sum of red and blue, N_{loss}). The total HNO₃ adsorbed on ice corresponds to the hatched area between the green and the black trace (N_{alpha-NAT}). The colorcoded labels correspond to the FTIR spectra in the upper panel. The figures on the bottom row show the FTIR absorption spectra of alpha-(left) and beta-NAT (right) at 182 and 192 K, respectively. The spectrum of the H_2O/ice NAT mixture (red) is deconvoluted into the pure H_2O ice (blue) and alpha- and beta-NAT (green) spectra, respectively. Characteristic absorptions are labeled in the corresponding spectra.



The top figure to the right shows the ideal geometry for a six-moleculewater-ring adsorbed on {001} alpha surface.

The figure on the bottom to the right shows the structure of the strongest water adsorption sites for alpha-(right) and beta (left) NAT.

Simulations of adsorptions of different water molecule conformations show that the largest calculated adsorption energy is nearly twice as high for alpha NAT in comparison to beta NAT.







Conclusion:

• alpha NAT - ice interaction is energetically more favorable than beta NAT - ice interaction

• no amorphous liquid HNO₃/H₂O layer upon admission of HNO₃ to a pure thin ice film of micron-size thickness

• NAT - Growth: (I) formation of alpha-NAT (II) spontaneous conversion of alpha- to beta-NAT in a narrow temperature window of observation (187.5 – 195 K) (III) subsequent growth of beta-NAT

References

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