Metastable Nitric Acid Trihydrate: a Possible Constituent of Polar Stratospheric Clouds and Cirrus Clouds

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1. Introduction

Nitric acid trihydrate (NAT) is an important constituent of Polar Stratospheric Clouds (PSCs), where it either occurs as small crystalline particles or in a mixture with ice. In 2004 the National Oceanic and Atmospheric Administration (NOAA) also detected NAT in cirrus clouds and in contrails [1]. As a consequence and combined with the fact that the level of water vapor is much too high in these clouds, Gao et al. [2] have set-up a promising model, which explains at least theoretically the conditions in these high altitude ice clouds.

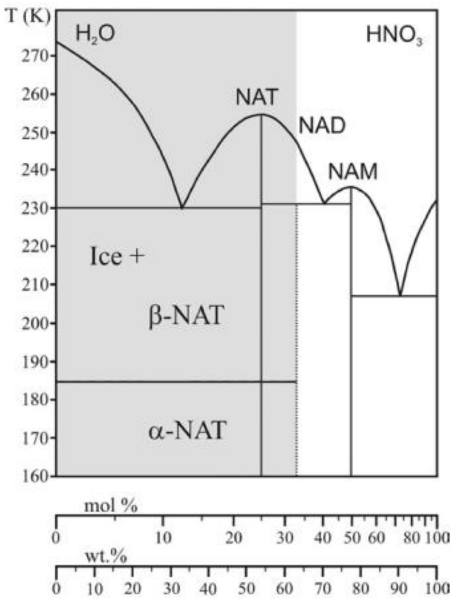

Figure 1 The phase diagram of nitric acid and water.

The idea of Gao et al. [2] was that in the upper troposphere it is not the thermodynamically stable and well-known hexagonal ice which is formed but the so-called *Ice of Complex Habit* (named *Delta Ice*). Here, the ice is a mixture of hexagonal ($P6_3/mmc$) and cubic ice ($Fd\bar{3}m$) and the surface of the solid particles is covered with NAT. The surface coverage suppresses the further growth of the crystalline particles, which in combination with the metastable phases leads to an elevated water vapor pressure and this is exactly what the field experiments have found.

Here we assume that it is not only the metastable ice phase (cubic ice) which contributes to the elevated water vapor but also that metastable NAT (alpha-NAT) might have the same effect. Interestingly, alpha-NAT has not been recognized by many atmospheric scientists and most papers in the field just focus on beta-NAT, which is thermodynamically stable. However, under the conditions of the lower stratosphere and the upper troposphere alpha-NAT can persist for several hours and when it occurs in a mixture with ice it can even stay for more than a day. Unfortunately, the crystalline structure of metastable alpha-NAT was unknown up to now, which has also hampered its spectroscopic identification.

2. Results and Discussion

Due to its metastability it was not possible to grow a single crystal of alpha-NAT, but a pure crystalline powder was accessible. However, it is a rather sophisticated procedure to deduce a crystalline structure from powder X-ray diffraction data. Nevertheless, we were successful in the present case and have for the first time solved the complete structure of alpha-NAT based on experiments and calculations. When comparing the new structure (monoclinic, $P2_1/a$ – see figure 2) critically with the known structure of the beta phase (orthorhombic, $P2_12_12_1$), one may recognize that the alpha structure exhibits much lower symmetry and a smaller cell volume.

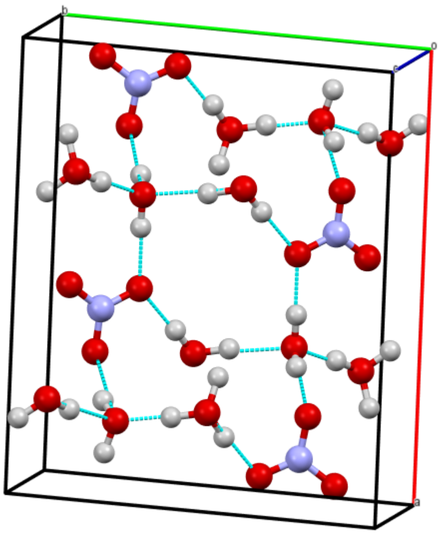

Figure 2 Unit cell of the alpha-NAT structure, axes: a-bright red, b-green, c-dark blue; spheres: oxygen-dark red, nitrogen-bright blue, hydrogen-grey; bonds: solid sticks-covalent bonds, turquoise dots-hydrogen bonds.

Other structures of lower symmetry might be possible. However, this structure fits both the X-ray and neutron diffraction data equally well, which were recorded independently on samples prepared in the same way. The refinement has been performed with the program package TOPAS 4.2 [3] and the conformities are extremely high.

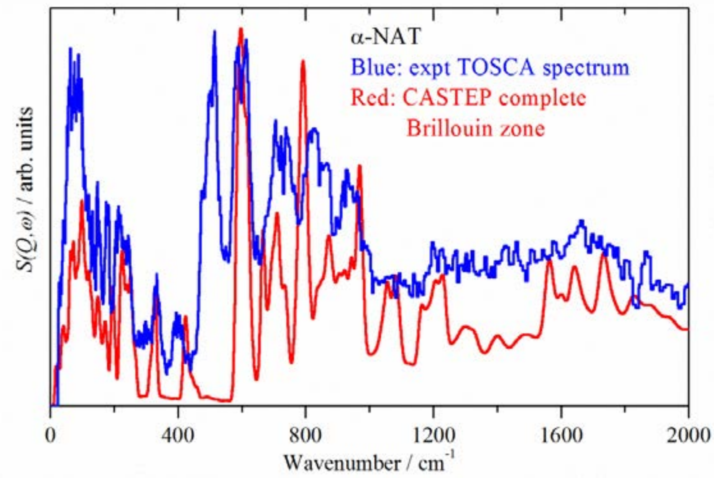

Figure 3 Inelastic Neutron Scattering spectra of alpha-NAT.

On the basis of the alpha structure the infrared (IR) and inelastic neutron scattering (INS) spectra have been calculated (figures 3 and 4). Here the band positions have been found with fair accuracy but the integral intensities are of rather modest accordance. The plotted bandwidth at half height used in figure 4 is just a self-constituted assumption. Most bands of the experimental spectrum are reproduced well. However, there is missing intensity at 530 cm^{-1} in figure 3. This band can be assigned to crystalline ice, which is present in all experiments.

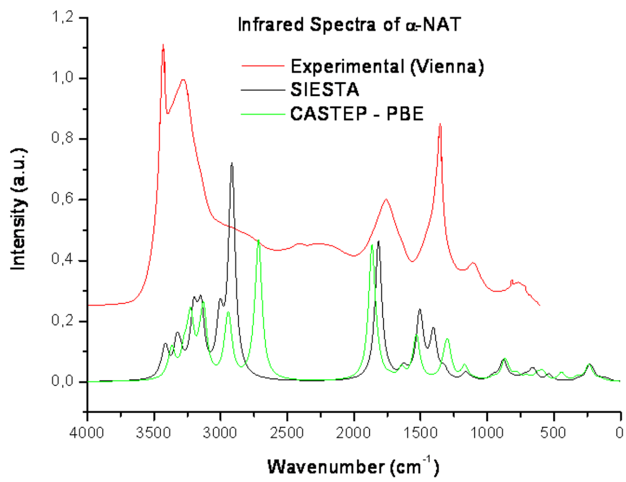

Figure 4 Experimental and calculated Infrared spectra of alpha-NAT.

The very narrow band at 3450 cm^{-1} (on the high energy side of the 3300 cm^{-1} band, figure 4) shows a characteristic pattern in all the infrared spectra. We assume that this band is not related to alpha-NAT but is due to small crystalline ice clusters as well. The reason that we never prepared alpha-NAT in its pure water-free form might be based upon its particular structure. In the center of this structure (see figure 2) is a hexagon formed by OH groups and water molecules, which in turn explains the high affinity of alpha-NAT and ice. In our former kinetic investigations we already found such an interaction between ice and alpha-NAT. We could show that an ice matrix can stabilize incorporated alpha-NAT crystals, which then can survive much higher temperatures than the pure form [4].

3. Conclusions

Metastable phases including cubic ice and alpha-NAT can partly explain the elevated water vapor pressure found in high-altitude ice clouds. In the past, alpha-NAT has however not been investigated to the same level as stable beta-NAT. We first solved the structure of alpha-NAT, which enabled the calculation of the vibrational spectra. Inconsistencies between experiment and calculation lead us to the conclusion that all alpha-NAT samples always contain small ice clusters, which certainly are responsible for the recorded spectral differences. In our former publications we found an interaction between ice and alpha-NAT which prolongs the lifetime of metastable NAT even at elevated temperatures. A possible explanation, we deduced now, is a water hexagon in the alpha-NAT structure, which favors interaction with ice.

Acknowledgments

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