ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment:	Metastable Nitric Acid Hydrates – Possible Constituents of Polar Stratospheric Clouds?	**Local Contact:**	Dr. St. Parker
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In the phase diagram of nitric acid and water exist two hydrate phases (nitric acid monohydrate (NAM) and nitric acid trihydrate (β-NAT)) – beside hexagonal ice and solid nitric acid. For the NAT, a metastable low-temperature modification (α-NAT) was found. Other metastable phases have been detected as well: cubic ice, two metastable modifications of nitric acid dihydrate (α-NAD and β-NAD), and a nitric acid pentahydrate (NAP).

We have developed a particular quenching technique in order to prepare amorphous ice and hydrate samples, from which we grow the respective crystalline phases, metastable and stable ones as well. Only recently, we have applied X-ray diffraction to verify the phase compositions of samples of different concentrations, to investigate the kinetics of the phase changes, and to determine the sizes of the crystallites. Additionally, the morphologies of the hydrate particles have been monitored by environmental scanning electron microscopy (cryo-ESEM). Vibrational spectra (FTIR and Raman) of the pure phases have been recorded and the data have been used for aerosol chamber experiments and satellite measurements. When comparing the FTIR and Raman data it became obvious that the spectral assignments of the different phases were incomplete. Therefore, ab initio molecular dynamics simulations of these solids have been carried out in order to support the assignments. The computer program SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) has been applied. However, these calculations have supplied only the band positions. Intensity values were available only for infrared spectra but not for Raman bands. Hence, an additional technique of vibrational spectroscopy was required, which is Inelastic Neutron Scattering (INS). This technique is particular suited to monitor all those vibrations which include a hydrogen atom in the respective atomic displacement, since hydrogen has the highest neutron scattering coefficient, the respective vibrations then exhibit enhanced intensities in the INS spectra.

Before starting the INS measurements, calculations of the INS spectra were carried out. The spectra of NAM and β-NAT have been predicted. In figure 1 and 2 the experimental spectra (black line) and the calculated spectra (red line) have been compared. Obviously the calculated spectra show a high degree of accordance, however, better calculations are on the way. The spectra of crystalline and amorphous samples are rather different. Particularly, the distinctive translational (< 400 cm^{-1}) and librational modes (< 800 cm^{-1}) give evidence that the crystalline substance has been formed.

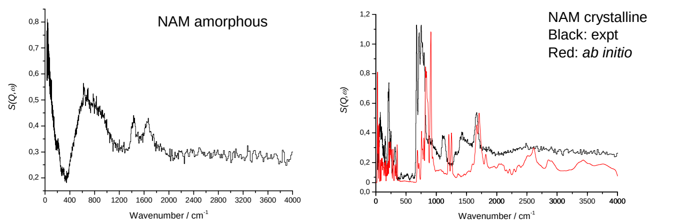

Figure 1: Nitric acid monohydrate (NAM) was crystallized from an amorphous sample at 160 K. The measurements were performed at 20 K. The INS spectrum of NAM was compared with a respective calculation.

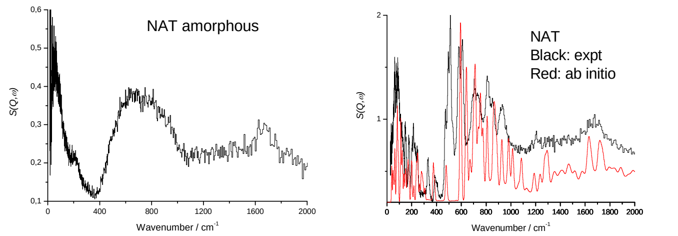

Figure 2: The stable modification of nitric acid trihydrate (β-NAT) was crystallized at 180 K from the amorphous sample. The spectrum of β-NAT shows good accordance with the calculation.

During our measurement term the neutron beam was closed down several times. Therefore, we have not finished the whole project. Measurements of α-NAT, α-NAD and NAP are still open. We would be very delight to get the chance to continue these measurements, since the first results are rather promising and further calculations of INS spectra will be presented duly for the next measurements. Additionally, we have developed a new sample carrier which will help us to safe time in the course of sample production.

The results will be presented in a PCCP paper which is in preparation just now and a conference contribution at the EGU assembly in Vienna has been accepted.

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