ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number:	RB820015		
Date of Report:	11.02.2009		
Title of Experiment:	Metastable Nitric Acid Hydrates – observing new phases	**Local Contact:**	Dr. St. Parker
Principal Proposer:	Dr. Hinrich Grothe	**Instrument:**	TOSCA
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Experimental Team:	Hinrich Grothe, Philipp Baloh	**Date of Experiment:**	2-7/12

In the phase diagram of nitric acid and water exist two stable 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). The existence of these phases has been proven by X-ray diffraction experiments. However, several vibrational data are still incomplete.

During this year's experiment we have completed our programme, which we had intended in our original proposal in 2007. Specifically, we have measured the spectra of each phase in the following sequences: nitric acid dihydrate (33 mol%): amorphous → β-phase, nitric acid trihydrate (25 mol%): amorphous → α-phase → β-phase, nitric acid pentahydrate (19 mol%): amorphous → NAP/ α-NAT/ice.

In order to safe time in the course of sample production, we have developed a new sample carrier, which we have combined with a particular spray-on-quenching technique. This new set-up gave us the opportunity to prepare larger amounts of amorphous samples, from which we could grow the respective crystalline phases, stable and metastable ones as well.

Only recently, 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 has been applied supplying the band positions. However, the band assignments were not complete. Therefore, we have carried out additional INS experiments. In figures 1-3 the experimental spectra (black line) of NAT, NAP and NAD have been presented. In the case of β-NAT the calculated spectrum (red line) has been compared, which shows an acceptable accordance. 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 different phase transitions occur.

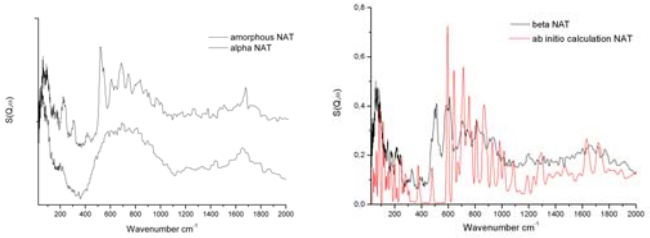

Figure 1: Nitric acid trihydrate (α-NAT) was crystallized from an amorphous sample at 160 K. The phase change into the stable high-temperature modification (β-NAT) occurred at 180 K. The measurements were performed at 20 K. The INS spectrum of β-NAT was compared with a respective calculation.

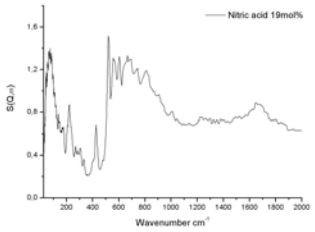

Figure 2: A mixture of metastable nitric acid pentahydrate (NAP), α-NAT and cubic ice were crystallized at 158 K from the amorphous sample.

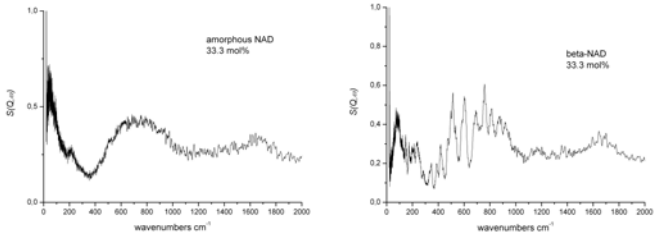

Figure 3: Metastable nitric acid dihydrate (β-NAD) was crystallized at 160 K from the amorphous sample.

A PCCP paper is in progress and a conference contribution at the EGU General Assembly 2009 in Vienna has been accepted.

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