Metastable Nitric Acid Hydrates – Possible Constituents of Polar Stratospheric Clouds

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Solid cryo-particles in the atmosphere are often not well-characterized concerning their phases which is due to a lack of respective online techniques. The only field measurements available so far are based either on vibrational spectroscopy or on aerosol mass spectroscopy. Neither of both have direct access to the phase composition of the particles, but depend on well-corroborated data from laboratory measurements. On the other hand, offline techniques like particle filters miss the goal due to the metastability of the cryo-particles.

It was the aim of our research to determine the phase composition of solid polar stratospheric clouds, i.e. PSC type Ia and II particles. Satellite measurements in cooperation with aerosol chamber experiments and laboratory studies have recently tried to identify the crystalline HNO_3/H_2O phases in question. Most studies favour the existence of stable nitric acid trihydrate (β-NAT) whereas much less is known about metastable phases. Therefore, our interest is focused on the latter, i.e. the low-temperature modification of nitric acid trihydrate (α-NAT), nitric acid dihydrate (α-NAD, β-NAD) and nitric acid pentahydrate (NAP). We have prepared these phases in a laboratory model using a quenching technique. The resulting samples are non-equilibrium amorphous solids from which particularly the metastable phases crystallize in an annealing procedure, which is due to their lower nucleation barriers. The crystallization behaviours of NAD [1] and NAT [2] have thus been investigated by X-ray powder diffraction. Those results have been used to corroborate the respective FTIR and Raman spectra [3]. Aerosol chamber experiments and theoretical calculations found evidence that the particle's morphology and crystalline orientation have strong impact on the vibrational spectra. That is why we have controlled for the shape of the particles in our samples by environmental scanning electron microscopy [4,5] and also found some clues concerning the crystallization kinetics. Current Raman spectra [6] show the extraordinary importance of the low-frequency region (20-200 cm^{-1}), which is particularly suited for phase differentiation.

[1] Tizek, H.; Knözinger, E.; Grothe, H. *Phys. Chem. Chem. Phys.* **2002** , 4, 5128-5134.
[2] Tizek, H.; Knözinger, E.; Grothe, H. *Phys. Chem. Chem. Phys.* **2004** , 6, 972-979.
[3] Grothe, H.; Lund Myhre, C.E.; Tizek, H. *Vibr. Spectr.* **2004**, 34, 55-62.
[4] Grothe, H.; Tizek, H.; Waller, D.; Stokes, D. J. *Phys. Chem. Chem. Phys.* **2006**, 8, 2232-2239.
[5] Grothe, H.; Tizek, H.; Ortega, I.K. *Faraday Discussion* **2008**, 137, 223-234.
[6] Grothe, H.; Lund Myhre, C.E.; Nielsen, C. J. *J. Phys. Chem. A* **2006**, 110, 1, 171-176.