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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-situ observations and modeling of nitric acid-containing particles in a cirrus cloud formation region" *by* C. Voigt et al.

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Response to anonymous referee 1

We thank the reviewer for his/her comments.

HNO_3 component of NOy in ice particles

We extensively discuss the measurement principle and the HNO_3 content in NOy in the gas phase and in particles in section 2 Instrumentation. Gamblin et al. (2006) discuss the non-HNO_3 constituent of NOy condensing on cirrus ice particles and suggest that HNO_3 is often a major component of NOy in ice particles. We changed the abstract and state clearly that water (H_2O) and reactive nitrogen species (NOy) have been measured. As the referee does not challenge the notion, that a large fraction of the NOy in particles is HNO_3, we want to keep the title in the form: In-situ observations

and modeling of small nitric acid-containing cirrus particles.

Trapping model

The trapping model suggests that the amount of HNO_3 in ice crystals is determined by the amount of HNO_3 contained in aerosol at the point of freezing plus HNO_3 in ice, initially adsorbed on the ice surface and partially trapped during ice crystal growth.

Partial capture of HNO_3 during aerosol freezing constitutes a small fraction of HNO_3 contained in small enough ice particles; most of the HNO_3 is taken up during growth - at low enough temperatures with a molar HNO_3/H_2O ratio equal to that in ambient air. Processes occurring on the ice surface such as diffusion or hopping of molecules in the ice surface layer or into the bulk ice, and desorption of molecules from the surface layer, which are not well constrained by laboratory measurements, appear in a single parameter, the trapping efficiency. It can be viewed as the ratio of an effective (meaning all surface-related processes enumerated above are included) desorption velocity of the HNO_3 molecules to the ice crystal growth rate.

In the absence of constraints on the trapping efficiency, we have fitted it (Kärcher and Voigt, 2006) along with a net ice growth rate to available atmospheric datasets (Voigt et al., 2006). Hence the trapping model is based on adsorption theory but additionally includes ice crystal growth. We find the application of a static adsorption model unsatisfactory in principle, as it ignores the dynamic component of ice growth (and evaporation), which is physical reality. The trapping concept does not automatically imply that all HNO_3 resides inside the bulk ice volume, it may well be kept at the surface during (relatively slow) growth. Situations are conceivable in which growth is slow – and in which the trapping model converges into a quasi-static adsorption approach. Details of the full trapping model are given in Kärcher and Basko (2004).

In sum, we view the trapping approach as a generalization of pure adsorption, there doesn't need to be a contradiction as perhaps suggested by the referee. In the slow growth cases, that are realized at least for low temperatures, it does not come as a

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complete surprise that a simple adsorption picture works, as noted by the referee. But again, only the trapping approach can tell how to calculate uptake properly in the common situations where ice crystal sizes and cirrus surface areas are continuously changing. We also feel that static adsorption experiments made in the laboratory provide one essential component to constrain uptake models.

Some laboratory measurements include growing ice surfaces and support that trapping or burial indeed takes place for HNO_3 (Diehl et al. (1995), Ullerstam and Abbatt (2005)). We agree with the referee that more detailed laboratory studies with growing ice surfaces are required to better constrain the trapping model and to achieve a true understanding of the basic mechanisms involved. We think this is the way to go, instead of using static adsorption models that have unconstrained parameters on their own and are less plausible to apply in cirrus conditions.

Gamblin B. et al. (2006): Nitric acid condensation on ice: 1. Non-HNO_3 constituent of NOy condensing cirrus particles on upper tropospheric, J. Geophys. Res., 111, D21203, doi:10.1029/2005JD006048

Kärcher, B. and M. M. Basko (2004): Trapping of trace gases in growing ice crystals, J. Geophys. Res., 109, D22204, doi:10.1029/2004JD005254.

Kärcher, B. and C. Voigt (2006), Formation of nitric acid/water ice particles in cirrus clouds, Geophys. Res. Lett., 33, L08806, doi:10.1029/2006GL025927.

Diehl, K., S. K. Mitra and H. R. Pruppacher (1995), Atmos. Environ., 29, 975-981.

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