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Atmospheric
Chemistry
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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.

Anonymous Referee #1

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This paper presents another set of measurements of the NOy content of cirrus cloud particles, to add to a growing set of similar measurements. The novelty of these measurements is that the particles sampled are quite small and at low temperatures, potentially consistent with the idea that the cloud was in the formation stage. This is always hard to determine - i.e. whether a cloud is forming or dissipating - but I am willing to accept the working hypothesis (page 1857) that the cloud was forming.

As with previous measurements of this nature, there is the uncertainty that arises when only NOy is measured and not HNO3 directly, and so the title of the paper should be changed. I don't challenge the notion that it is probably largely HNO3 that is in/on the particles but the authors should distinguish this work from that where HNO3 in/on the ice has been measured directly. There is also the potential for unidentified NOy

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components that could be in/on the particles, such as HNO4. The uncertainties that arise from the fraction of NOy that might be HNO3 are reasonably handled in the paper.

The paper asserts that the HNO3 mole fraction of the particles is determined by a trapping mechanism. The nitric acid originates from a supercooled HNO3-H2SO4-H2O solution that homogeneously freezes to form ice. The modeling in the paper contends that the HNO3 mole fraction of these particles is relatively high because the acid from the freezing particle has been trapped, and that the mole fraction will go down as the particle grows. This interpretation builds upon earlier modeling studies that some of the authors have recently published. It is an interesting idea and stands in contrast to the earlier contention that the amount of nitric acid in the ice particle is all at the surface and that the amount can be described by a dynamic equilibrium with the gas phase. In my opinion, the jury is still out as to which model is correct - perhaps both are applicable in different circumstances. What can be said is that the trapping model is essentially unconstrained by controlled laboratory measurements, i.e. we do know that nitric acid can be buried but we don't know the timescale for buried nitric acid to be released from the ice. The surface adsorption model also has its uncertainties, in particular with respect to the degree that equilibrium is maintained as the ice is growing or evaporating.

So, I think it is unwise to put all of one's eggs in one ("trapping") basket and to disregard the surface adsorption model. A simple addition to the paper would be to analyze the data in this manner also. I did a simple calculation to justify why I think this. For the particle pressures of HNO3 encountered, the new laboratory measurements at this temperature indicate a surface coverage of about 2 times 10ˆ14 molecules/cm2 (Ullerstam et al., Faraday Disc., 2005). I calculate that for this surface coverage and for an ice particle 5 microns in radius, the HNO3 mole fraction would be 4 times 10ˆ-5, i.e. essentially the observed value. Indeed, the general trends in the observations (see Voigt et al., GRL, 2006) are qualitatively consistent with the new laboratory measurements (Ullerstam et al., Faraday Disc., 2005) for surface adsorption, showing decreasing uptake at higher temperatures, saturation at values similar to this reported mole fraction, and somewhat decreased uptake at very low partial pressures.

In summary, I would like to see these results published in ACP and I think the trapping model is an interesting addition to this subject. However, until we know more, I suggest a somewhat broader interpretation of the results.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1849, 2007.

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