

Interactive comment on “Laboratory evaluation of the effect of nitric acid uptake on frost point hygrometer performance” by T. Thornberry et al.

Anonymous Referee #2

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In this manuscript, Thornberry and co-authors present and discuss laboratory investigations of the nitric acid uptake to the frost layer of a chilled mirror hygrometer and its effect on the measured frost point temperature. For the laboratory studies, the authors have adopted the setup of the well developed and established Cryogenic Frost Point Hygrometer (CFH) frequently flown on balloons to measure water profiles from the surface to the middle stratosphere with high sensitivity and accuracy. Motivation for the laboratory study were remarkable deviations between different water measurement methods in particular at mixing ratios below 10 ppm measured in the tropical tropopause region and the lower stratosphere. Up to now it seems unclear what causes

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these discrepancies. Therefore, it is an important task to systematically investigate instrument performance and accuracy, as the authors of the present manuscript did in an exemplary way. The paper is well-structured and clearly written, with a concise introduction to the topics, a comprehensive description of experimental methods, and a clear presentation and discussion of results and implications.

The paper is well in the scope of AMT. In my mind it can be accepted as is. For preparing the final version, the authors may consider just a few remarks and minor corrections listed below.

My main question concerns the discussion of the amount of adsorbed nitric acid. It is interesting to see that this amount was increasing during continuous exposure of the frost layer to nitric acid. Based on this result the authors state that the nitric acid uptake did not reach equilibrium conditions, whereas this equilibrium is assumed for the uptake of water molecules, which of course is prerequisite for a proper frost point measurement. But would equilibrium with respect to water uptake necessarily include a constant mass of the frost layer on the mirror? What about slight drifts of the condensed mass caused by the temperature control cycles? Would it be possible in further experiments to evaporate the accumulated frost layer from the first instrument and measure its mass with the second, or with another water detector in series to the CFH, similar to the measurement of the nitric acid mass with the NO_y instrument? What if the frost mass slightly increased during the exposure experiment with co-condensation of nitric acid? What is known about the thickness of the frost layer at all? I assume that it is something like hundreds of monolayers or even more. This would mean that the molar fraction in the layer is very low and may be explained by adsorption / desorption processes. Kärcher and Voigt (Geophys. Res. Lett. 33, 2006) reported molar fractions of about 10^{-5} at 195 K in natural cirrus. During the exposure experiments the frost temperature was even lower, which means that the molar fraction of nitric acid uptake into the ice phase is even higher than 10^{-5} . This may explain the amount of nitric acid, but probably not yet the almost linear increase with exposure time. This is puzzling,

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and it would really be nice to also measure the water mass in the layer, and thereby the molar ratio.

I would also like to comment on the existence of nitric acid trihydrate (NAT) phases locally on the mirror the authors suggested in section 3.3 of the manuscript. First of all, I would prefer to include both the trihydrate and dihydrate (NAD) phases in the discussion here. Anyway, let us discuss the formation and growth of nitric acid hydrates. The authors mention that the gas-phase above the mirror is supersaturated with respect to the hydrates. So, once formed, the hydrates should continue to grow during the exposure experiments. It would be important to know the mass growth rates of such hydrate germs or nuclei. In line 23 of page 3736 it is stated that 'the adsorption rate of NAT is likely to be too small to allow NAT to effectively control the mirror reflectivity'. My first question here would be whether the mass growth rate would be in the range of the measured increase of nitric acid mass on the mirror. For the conditions of the exposure experiment (temperature 180 K, pressure 128 hPa, 1.9 ppb nitric acid) I quickly estimated a nitric acid kinetic molecular flux of 200 ng per hour to a surface of 1 mm². I leave it to the authors to estimate the diffusion limited flux to the mirror surface, which certainly is more appropriate here. Another hint on the question whether hydrates formed on the mirror could come from the actual saturation ratio with respect to NAD and NAT. I would suggest the authors to mention in the final paper the actual saturation ratios and to include an estimate of the net diffusional flux of nitric acid molecules towards the mirror surface. This flux strongly depends on the fate of nitric acid molecules at the surface, but already an upper limit of the flux with the assumption of zero concentration at the surface, i.e. infinite uptake, could be helpful for understanding the details.

I suspect that the authors already thought about or already conducted more exposure experiments at higher nitric acid mixing ratios and higher frost point temperatures to further investigate the open questions of nitric acid uptake and hydrate formation on the mirror. As stated above, I recommend to also measuring, if possible, the water

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mass as a function of exposure time.

Minor Comments:

Page 3727, line 29: Instead of referring to the lower troposphere and the region above the lower troposphere you may better refer to temperatures above and below 0 C.

Page 3728, lines 17 to 19: Another important condition needs to be fulfilled, namely the condensate surface temperature to equal the measured mirror temperature.

Page 3731, line 18: Replace ID with inner diameter, or explain at first occurrence.

Page 3731, line 24: Mention the temperature and pressure the standard flow is calculated for.

Page 3733, line 8: in the flow system

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 3725, 2010.

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