



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

**T. Thornberry et al.**

troy.thornberry@noaa.gov

Received and published: 21 December 2010

We thank the reviewer for the review of our manuscript and the thoughtful and constructive questions raised. We have used the comments to revise the manuscript where possible while not significantly expanding the scope of the discussion beyond the focus of the current paper. Responses to individual comments are included 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?*

The signal that is maintained constant in the frost point hygrometer is the reduced reflectivity of the mirror surface, which does not rule out the possibility that the water mass on the mirror changes over time as the frost on the surface anneals or slowly sublimates around the edge of the mirror due to a microgradient in mirror temperature from the center to the edge. Visible monitoring of the mirror surface with the microscope showed there did not appear to be major changes except during the longest duration experiments (> 6 hours) when a clear area around the mirror edge became visible.

*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<sub>y</sub> instrument?*

We did look at the signal on the downstream frost point instrument when we evaporated the frost layer from the upstream instrument. The frost layer evaporation occurs rapidly (~2 s for the frost to visibly disappear) with the existing software, which produces a transient that cannot be resolved by the downstream instrument. We have considered options of slowing the evaporation or using a faster measurement downstream and hope to address this in future experiments and publications.

*What if the frost mass slightly increased during the exposure experiment with co-condensation of nitric acid?*

Any increase in the frost mass is likely to be fractionally small since there is no

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

significant change in the appearance of the mirror frost layer over the course of an exposure experiment and it is certainly not increasing proportionally with the increase in nitric acid mass (factor of 10 increase between 10 and 120 minute exposures).

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

The electron micrographs in Leu and Keyser (2009), particularly Figure 6, provide evidence of what the likely frost layer morphology on the mirror is—a rough surface with semi-discrete structures and sharp edges. This makes sense since the frost layer needs to be scattering in order to produce the required reduction in surface reflectivity. Unlike in a natural cirrus cloud, we are providing a continuous supply of  $\text{HNO}_3$  available for adsorption. Given the roughness of the frost surface and the results of flow tube studies of  $\text{HNO}_3$  uptake at low temperatures (reviewed in Abbatt, 2003), the approximately linear uptake is not surprising when considered from a surface area coverage basis. We agree that a frost layer water mass measurement combined with the nitric acid mass to produce a molar ratio would be an important measurement for assessing the state of the frost layer with increasing exposure.

*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*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



*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'.*

We have removed the sentence “However, due to the low mixing ratio of  $\text{HNO}_3$  in our case, the adsorption rate of NAT is likely too small to allow NAT to effectively control the mirror reflectivity.” which is tangential to the arguments of the paper and does not adequately address the potentially complicated issues related to mirror reflectivity control on a multi-component condensate dependent on co-deposition, which are beyond the scope of the current manuscript.

*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 mm<sup>2</sup>. 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.*

A diffusive flux calculation over the depth of the (idealized) 1 mm boundary layer depth

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



yields a mass accumulation rate similar to the observed uptake, but the assumptions and approximations necessary to allow a simple calculation limit the significance of the agreement. From the H<sub>2</sub>O-HNO<sub>3</sub>-hydrate equilibria reported in Hanson and Mauersberger (1988) and Worsnop et al. (1993), we have calculated the HNO<sub>3</sub> supersaturation with respect to NAT and NAD for our experimental conditions. For the conditions of the experiment in Figure 5, the mirror temperature is ~5.5 K below the calculated NAT saturation temperature, producing a HNO<sub>3</sub> supersaturation  $P/P_{sat}$  ~60. The calculated  $P/P_{sat}$  for NAD (from Worsnop et al, 1993) is ~7, but the very high value for NAT indicates that NAD would convert rapidly to NAT (Worsnop et al., 1993). Text has been added to indicate the calculated NAT supersaturation.

*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 mass as a function of exposure time.*

We also feel that these are obvious directions for follow-on experiments to take and we hope to, when time permits, pursue further investigations along these and other lines.

*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.*

We have changed the text to reflect temperatures above and below 0 °C. The actual change from dew point to frost point measurement generally takes place at a dew point temperature below 0 °C. Balloon CFH instruments are typically programmed to burn off the condensate layer and reform it at a mirror temperature below –20 °C to ensure the condensate layer is frost and not supercooled liquid.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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

This is indeed a necessary condition to avoid a measurement artifact and we considered whether there could be any effect from insulation by the condensate layer. Given any reasonable estimate of the thickness of the frost layer and the relative thermal transfer to the frost from the mirror and the air (as well as the near-surface temperature of the air based on the simple thermal boundary layer calculation) combined with the thermal conductivity of ice/frost, the potential temperature difference across the depth of the frost layer is negligible ( $< 0.1\text{ }^{\circ}\text{C}$ ).

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

Text changed to read: “inner diameter (ID)” at first usage and “ID” thereafter

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

Information added in text: (0  $^{\circ}\text{C}$ , 1013.25 hPa)

*Page 3733, line 8: in the flow system*

Corrected.

---

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

