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Interactive comment on "Heterogeneous Kinetics of H_2O, HNO_3 and HCl on HNO_3 hydrates (α-NAT, β-NAT, NAD) in the range 175–200 K" *by* Riccardo Iannarelli and Michel J. Rossi

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Dear Colleagues,

We read with interest the results of your recent experiments investigating the kinetics of H_2O and HNO_3 (and HCl) on NAT. We would like to offer some comments on the portion of the manuscript that discusses chilled mirror hygrometers and our recent manuscript "Persistent Water-Nitric Acid Condensate with Saturation Vapor Pressure Greater than That of Hexagonal Ice"

Lines 855-865: Initial development of a frost-point hygrometer for measurement of water vapor in the UTLS was reported by Brewer et al. (1948). Numerous papers in

the scientific literature from the 1950s to present describe further instrumental developments and variations, characterize performance, and analyze results from chilled mirror hygrometer measurements of UTLS H_2O. Chilled mirror hygrometers have been used for decades on balloon sondes at locations around the world (e.g. Hurst et al., 2011). The instruments used in our studies are laboratory versions of the CFH (cryogenic frostpoint hygrometer) described by Vömel et al. (2007). Thornberry et al. (2011) describes details of the implementation of the CFH for our specific experiments.

Line 862-863: "increase in scattering because of the formation of a polycrystalline ice deposit" would be better described as "increase in scattering due to growth of the polycrystalline ice deposit"

Lines 866-872: The relevant conclusion from Thornberry et al. (2011) is that the lack of perturbation to the CMH temperature (relative to the control) from the accumulation of HNO_3 on the mirror implies that there was no change in the H_2O saturation vapor pressure over the mirror condensate. This is reasonable, and not inconsistent with the results presented in the manuscript, given that the small amount of condensed HNO_3 and the high surface area of the polycrystalline frost result in incomplete frost surface coverage by HNO_3.

Lines 872-879: The TDL-based hygrometer that we recently developed for UTLS measurements (Thornberry et al., 2015) is not related to our laboratory frostpoint studies. As noted, it uses absorption spectroscopy to measure gas-phase H_2O (as do a number of other hygrometers used on research aircraft, e.g. JLH, DLH, VCSEL, HAI) and is not relevant to the present discussion and we suggest that this paragraph be omitted to avoid confusion. If you continue to include this discussion, we suggest 'Fahey and coworkers' be replaced by 'Thornberry, Rollins and coworkers'.

Lines 880-890: To clarify the typical experimental sequence in our HNO_3-ice experiments using the frostpoint hygrometer reported in Gao et al., (2016):

1. Pure ice frost layers were established on both CMH mirrors in a low-pressure flow

with a stable H_2O mixing ratio < 10 ppm.

2. HNO_3 was added to the flow between the two CMHs such that the flow past the second mirror contained 80-100 ppb HNO_3.

3. After a period of time (~1 hour in the experiment shown in Gao et al.), the temperature of the exposed mirror began to increase. The deviation increased with continued HNO_3 exposure until it stabilized at a temperature similar to the saturation temperature of NAT for the H_2O and HNO_3 partial pressures in the flow.

4. When the mirror temperature was stable, the H_2O mixing ratio in the flow (past both mirrors) was increased (to ~80 ppm in the experiment shown in Gao et al.) causing the temperatures of both mirrors to increase. The temperature of the HNO_3-exposed mirror stabilized at the NAT saturation temperature for the new H_2O partial pressure.

5. The HNO_3 addition was shut off. HNO_3 in the flow dropped by an order of magnitude in the first two minutes and then continued to decrease more slowly (double exponential decay with time constants of several minutes and greater than 30 minutes). The HNO_3 mixing ratio in the flow continued to decrease, but remained above the background level for the length of the experiments. The temperature of the HNO_3-exposed mirror began to decrease immediately upon removal of the HNO_3 addition, but more slowly than the calculated NAT saturation temperature, indicating a kinetic limit to the response of the condensate to HNO_3 in the gas phase. After ~1 hour, the temperature of the exposed mirror reached that of the control (unexposed) mirror, ~213 K in the experiment shown in Gao et al.

6. Instead of restabilizing when it reached the pure water ice saturation temperature, the temperature of the exposed mirror continued to decrease, suggesting that the H_2O vapor pressure of the condensate had become larger than that of pure H_2O ice. The depression in the mirror temperature relative to the control was sustained though multiple changes in H_2O amounts in the flow that caused the temperatures of both mirrors to increase or decrease by more than 5 °C, indicating that the condensate properties were stable even following loss and uptake of water. The HNO_3 measured downstream of the mirror varied with the mirror temperature (the temperature of other surfaces in the system remained unchanged), providing additional evidence of the continued evolution of HNO_3 from the mirror. Forced evaporation of the condensate in some experiments confirmed the continued presence of HNO_3 on the mirror.

Lines 891-899: In Gao et al. (2016), we make no statements about the relative evaporation rates of H_2O and HNO_3 from the mirror condensate (initially NAT), but argue that there is a continuing loss of HNO_3 from the condensate relative to H_2O due to the lack of HNO_3 in the air flow while the H_2O flux from the mirror is balanced by a flux to the condensate from the gas phase. We argue that the elevated vapor pressure of the condensate is indeed due to the presence of residual HNO_3 in the condensate that prevents the complete recrystallization of mirror H_2O into hexagonal ice.

Lines 899-920: It is likely that changes in the refractive index due to changes in condensate composition as well as changes in condensate morphology (crystal size and shape and surface roughness) play a role in changing the relationship between the mass of condensate on the mirror and the diffuse reflectivity. However, the frostpoint hygrometer is inherently a steady state instrument, and when a stable relationship between the mass of the condensate and the reflectivity exists, be that pure hexagonal ice, NAT, or another form, the mirror reflectivity-temperature feedback will operate to maintain a constant mass on the mirror and the mirror temperature will therefore reflect the saturation vapor pressure of the reflection-controlling condensate. This can be seen in the transition of the ice frost layer to NAT in the first part of our laboratory experiments where the mirror temperature rises from ice saturation to that of NAT, but then is stable at the NAT saturation temperature regardless of the difference in refractive index between ice and NAT. For the HNO_3-H_2O condensate with a lower H_2O saturation temperature than pure ice that occurs in our experiments following the loss of some fraction of the HNO_3 from the NAT frost, the mirror temperature transitions to the lower value over a period of hours and then remains stable for many more hours, even as

HNO_3 continues to evolve from the mirror condensate. Additionally, the experiments in which the water vapor in the flow over the condensate was changed demonstrate the H_2O vapor pressure control of the condensate as well as the stability of the condensate over a range of temperatures. Changes in condensate optical properties due to changes in composition or morphology that produce a change in the reflectivity would be interpreted by the CMH feedback control as a change in condensate mass and drive a compensating change in mirror temperature to restore the reflectivity to its set value. The temperature perturbation would only last until the resulting change in the condensate mass restored the original reflectivity, after which the mirror temperature would adjust to the saturation temperature necessary to maintain the condensate in steady state. Only a continuous change in the optical properties of the mirror condensate could produce an extended offset in the mirror temperature from the condensate saturation temperature.

Regards,

Troy Thornberry, Andrew Rollins, Ru-Shan Gao and David Fahey

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