

***Interactive comment on “Heterogeneous Kinetics of H<sub>2</sub>O, HNO<sub>3</sub> and HCl on HNO<sub>3</sub> hydrates ( $\alpha$ -NAT,  $\beta$ -NAT, NAD) in the range 175–200 K” by Riccardo Iannarelli and Michel J. Rossi***

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Received and published: 31 May 2016

Dear Colleagues,

We read with interest the results of your recent experiments investigating the kinetics of H<sub>2</sub>O and HNO<sub>3</sub> (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

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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<sub>2</sub>O. 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<sub>3</sub> on the mirror implies that there was no change in the H<sub>2</sub>O 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<sub>3</sub> and the high surface area of the polycrystalline frost result in incomplete frost surface coverage by HNO<sub>3</sub>.

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<sub>2</sub>O (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<sub>3</sub>-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

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with a stable H<sub>2</sub>O mixing ratio < 10 ppm.

2. HNO<sub>3</sub> was added to the flow between the two CMHs such that the flow past the second mirror contained 80-100 ppb HNO<sub>3</sub>.

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<sub>3</sub> exposure until it stabilized at a temperature similar to the saturation temperature of NAT for the H<sub>2</sub>O and HNO<sub>3</sub> partial pressures in the flow.

4. When the mirror temperature was stable, the H<sub>2</sub>O 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<sub>3</sub>-exposed mirror stabilized at the NAT saturation temperature for the new H<sub>2</sub>O partial pressure.

5. The HNO<sub>3</sub> addition was shut off. HNO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>-exposed mirror began to decrease immediately upon removal of the HNO<sub>3</sub> addition, but more slowly than the calculated NAT saturation temperature, indicating a kinetic limit to the response of the condensate to HNO<sub>3</sub> 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<sub>2</sub>O vapor pressure of the condensate had become larger than that of pure H<sub>2</sub>O ice. The depression in the mirror temperature relative to the control was sustained though multiple changes in H<sub>2</sub>O 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

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were stable even following loss and uptake of water. The  $\text{HNO}_3$  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  $\text{HNO}_3$  from the mirror. Forced evaporation of the condensate in some experiments confirmed the continued presence of  $\text{HNO}_3$  on the mirror.

Lines 891-899: In Gao et al. (2016), we make no statements about the relative evaporation rates of  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  from the mirror condensate (initially NAT), but argue that there is a continuing loss of  $\text{HNO}_3$  from the condensate relative to  $\text{H}_2\text{O}$  due to the lack of  $\text{HNO}_3$  in the air flow while the  $\text{H}_2\text{O}$  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  $\text{HNO}_3$  in the condensate that prevents the complete recrystallization of mirror  $\text{H}_2\text{O}$  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  $\text{HNO}_3$ - $\text{H}_2\text{O}$  condensate with a lower  $\text{H}_2\text{O}$  saturation temperature than pure ice that occurs in our experiments following the loss of some fraction of the  $\text{HNO}_3$  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

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$\text{HNO}_3$  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  $\text{H}_2\text{O}$  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

#### *Additional References*

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Hurst, D. F., S. J. Oltmans, H. Vömel, K. H. Rosenlof, S. M. Davis, E. A. Ray, E. G. Hall and A. F. Jordan (2011) Stratospheric water vapor trends over Boulder, Colorado: Analysis of the 30 year Boulder record, J. Geophys. Res.-Atmos., 116, D02306, doi:10.1029/2010JD015065.

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