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Atmospheric Chemistry and Physics Discussions

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 Colleague,

We thank you very much for the detailed report on our paper dealing with kinetic and thermodynamic aspects of binary and ternary hydrates of HNO3 and HCl under UT/LS conditions. As advised by Referee 2 we have decided to remove the entire section on the background section of the Cryogenic Mirror Hygrometer (CMH) as we recognize that we do not have sufficient expertise in this area. However, we have written a new section at the end of the "Conclusions and Atmospheric Implications" Section (5) focusing on your newest experiments (Gao et al., 2016) and how it fits together with the kinetic results of the present study. We have been guided by the succinct description of

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your experiment in your Interactive Comment that helped us to define and sharpen the salient points of your experiment. We have come to the conclusion that your observations are entirely consistent with the rates of evaporation of HNO3 and H2O measured in the present study when we extrapolate our rates to the temperature range of interest in your newest study, namely 207-213 K. We therefore do not have a point of contention with the conclusions of above-referenced paper anymore and thought it to be worthwhile to point this out at the end of our report even though we cannot make a guess as to the nature of the “second condensate” that must await further investigations.

Below you will find the significant insert into the text of the present paper:

At last it is useful to view the outcome of a recent laboratory experiment dealing with the binary HNO3/H2O system monitored using a cryogenic mirror hygrometer (CMH) (Gao et al., 2016) in light of the present kinetic results. In the basic experimental setup the behavior of the sample CMH exposed to a combined low pressure H2O/HNO3 flow is compared to the response of a reference CMH that is located upstream of the HNO3 source and exposed to the H2O flow alone, and has been described in detail by Thornberry et al. (2011). Any increase in scattering of the incident monitoring laser beam owing to growth of the polycrystalline ice deposit will be counterbalanced by heating of the mirror to bring back the optical detector signal to a predetermined set point. The typical experimental sequence in Gao et al. (2016) starts by establishing pure ice frost layers on both CMH mirrors at a stable mixing ratio of < 10 ppm after which a continuous flow of HNO3 was added such that the flow past the sample CMH contained 80-100 ppb HNO3.

After typically one hour the gradual build-up of a NAT layer on the CMH was accompanied by a temperature increase of the sample CMH to settle around the saturation temperature Tsat of NAT at the chosen H2O and HNO3 flow rate. An increase of the H2O flow from 6 to 80 ppm led to ice growth on both mirrors accompanied by an increase of Tsat of NAT adjusting to the new H2O flow rate. Suddenly, the HNO3 flow was shut off which first led to a rapidly decreasing MS signal for HNO3 but ending up in

an above background signal corresponding to 0.5 to 1.0 ppb HNO3. The temperature of the sample CMH continued to decrease below Tsat of pure ice monitored by the reference CMH suggesting that Peq(H2O) of the condensate had become larger than that of pure ice. This solid state on the sample CMH was called “second condensate”. The low level of HNO3 continued to react to repetitive increases (CMH heating) and decreases (CMH cooling) of the H2O flow in a reproducible manner all the while staying below the level corresponding to Tsat of pure ice on the reference CMH. These repetitive H2O on-off sequences provided additional evidence of the continued evaporation of HNO3 from the condensate. The response of HNO3 leaving the condensate undersaturated with respect to NAT is at first sight certainly unexpected based on the results displayed in Figures 2b and 4b. However, if one considers the relatively high mirror temperatures ranging between 207 and 213 K between which the “second condensate” was cycled by way of changing the H2O flows it suddenly becomes conceivable that Rev(HNO3) becomes equal to Rev(H2O) in that temperature range. Linear extrapolation of the absolute rates of evaporation hints at similar magnitude for temperatures exceeding 210 K beta- NAT (Figure 4). For alpha-NAT the temperature at which the evaporation rates of H2O and HNO3 become equal is even below 200 K owing to a steeper T-dependence of Rev(HNO3) in alpha-NAT (Figure 2 and Table 4). We conclude, that the observed dynamics of the experiment performed by Gao et al. (2016) is entirely consistent with the kinetic results of the present study. However, the results of the Gao et al. (2016) laboratory experiment would certainly be different at lower temperatures more representative of the UT/LS.

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