

## ***Interactive comment on “HONO and NO<sub>2</sub> evolution from irradiated nitrate-doped ice and frozen nitrate solutions” by T. Bartels-Rausch and D. J. Donaldson***

### **Anonymous Referee #2**

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The authors present simple experiments that examine the effect of irradiation of ice surfaces that have been exposed to HNO<sub>3</sub>. The goal was to derive photochemical parameters describing the release of NO<sub>2</sub> and HONO. Although the authors observe release of both species, the results appear to be very qualitative and several parameters appear to be poorly defined. One has the impression that this was a hurried and rather limited set of experiments. There are many questions that need to be answered if this short study is to be fully published.

P10715, L12 The HNO<sub>3</sub> surface coverage is not measured in this work. It is calculated based on "well known" adsorption isotherms. The fact is that the equilibrium adsorp-

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tion of HNO<sub>3</sub> on an ice surface is anything but well defined. Experiments (including ones from Toronto) have shown that a significant part of the apparent surface accommodation is actually diffusion into grain boundaries. As shown in the comments below, the authors present almost no data enabling analysis of the surface state. There are e.g. no HNO<sub>3</sub> concentrations listed with the associated surface coverage (for a given T) and no mention of total exposure time. Recall that the HNO<sub>3</sub> uptake does not cease at equilibrium coverage as surface concentrations are depleted due to bulk transport. I would contend that the NO<sub>2</sub> and HONO seen are not simply the result of ice-surface photochemistry, but that significant amounts of HNO<sub>3</sub> dissolved in super cooled water in grain boundaries etc will have taken place. Parameters like the surface radiation flux, the depth of penetration of the radiation into the ice, the crystalline / morphological state of the surface are important to assess this, yet are not provided.

P10715, L23 The picture of the apparatus which I have from reading this is a simple "cup" containing ice at the bottom. A Figure would be useful to expand this. I would also like to know a little about the flow dynamics in such a system. It is clearly not a well defined flow tube and I wonder if the gas-transport to the surface is at all characterised ? How can the assumptions about the surface coverage of HNO<sub>3</sub> be validated in such a system ? How much HNO<sub>3</sub> may be lost on cold surfaces that are not ice ?

P10716, L9 There is too little information about the ice surface. At what temperature or cooling rate was the H<sub>2</sub>O frozen. In the absence of any real diagnostic tests, can the authors comment on how the ice at least appeared to the eye. I calculate that the ice film is very thick (about 1 mm), which normally means that freezing results in cracking. Was the surface very polycrystalline ? Would have annealing the ice have changed the results ? Why wasn't this tested ?

P10716, L13 "The mixture was prepared and stored in a glass bulb by freeze pump thaw cycles" Bad word order: Suggestion: "The HNO<sub>3</sub> was prepared by freeze pump thaw cycles of a 3:1  $\dot{E}$ . prior to dilution and storage in a glass bulb" What was the mixing ratio of HNO<sub>3</sub> in He and how was this prepared ?

P10716, L15 The 10 wt % HNO<sub>3</sub> / H<sub>2</sub>O mixture used to make frozen nitrate solutions cannot be described as "dilute". What thermodynamic state of HNO<sub>3</sub> / H<sub>2</sub>O actually freezes out in equilibrium. Do you even have ice + HNO<sub>3</sub> or is NAT stable. This information is critical to assess what chemistry the experiments have explored.

P10716, L27 Knowing that it was a 1000 W Xenon lamp does not help much. What was the photon flux at the surface ? This can be easily measured by actinometry or physically and in a photochemistry experiment it must be characterised.

P10717, L9 range of exposures = range of concentrations ?

P10717, L11 The concentrations of HONO, NO<sub>2</sub> and HNO<sub>3</sub> were not calibrated but calculated based on their relative reactivity with SF<sub>6</sub><sup>-</sup> ions. Although this will give you a ball-park number it does not take into account things such as mass dependent ion transmission efficiencies. In fact, the concentrations seem to be relative to that of HNO<sub>3</sub>, which itself is based on manometric dilution and, when we consider how sticky HNO<sub>3</sub> is, will have large uncertainty due to poorly characterised mixing ratio and transfer efficiency through glassware. HONO and (especially) NO<sub>2</sub> are really not difficult to calibrate and I am surprised that this was not done. Again, the impression of a quick-and-dirty set of experiments is reinforced.

P10718, L4 Here we need to know what concentrations of HNO<sub>3</sub> were used which resulted in the surface concentrations quoted. Was this parameter varied systematically or accidentally to get the spread of apparent coverages? How long do the authors wait until they think that the ice is in equilibrium with the HNO<sub>3</sub> from the gas phase (do they monitor hno<sub>3</sub> in this time ?). What combinations of HNO<sub>3</sub> concentration and temperature were employed ? How about some information pertaining to the ice-HNO<sub>3</sub> phase diagram ? Were all experiments in the ice-HNO<sub>3</sub> stability regime ?

P10718, L8 Gas-to-surface partitioning of HNO<sub>3</sub> is taken from (not from) Ullerstam et al. The authors must however be aware that these data have been reanalysed (Cox et al) to show that significant amounts of the uptake were due to bulk diffusion. i.e.

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the HNO<sub>3</sub> is not only on the surface. As mentioned already above, the experiments presented will explore not only surface adsorbed HNO<sub>3</sub> but also that dissolved in the super cooled water in e.g. grain boundaries. This is especially the case for thick (and probably cracked) ice surfaces as used here.

P10718, L24 "Several mono-layers (of H<sub>2</sub>O) condense and evaporate per minute". The rate of condensation and evaporation will actually be hundreds or thousands per second, depending on temperature. This statement should be made more quantitative and refer to the actual temperatures used. In addition, (as mentioned above) we need to know about the surface morphology / crystallinity. Even if the authors have applied no diagnostics they should at least present arguments as to why their ice films are comparable to those of Ullerstam et al., from whom they take the surface coverages.

P10719, L7 What is the flush time for gas in the ice-cell. How does this effect the HONO (or NO<sub>2</sub>) response times to switching light on/off.

P10719, L12 There are significant changes in ice surface between 193 and 253 K. Apart from vastly different rates of evaporation/condensation there is the question of the QLL, diffusion rate coefficients and also the amount of grain boundaries and super cooled liquid will change. It seems therefore unreasonable to state that the temperature dependence of HONO release is only a result of its surface adsorption. In this sense, the derivation of an activation barrier for HONO appearance is an over-interpretation of the data.

P10720, L16 "Diffusion from the ice was negligible as HNO<sub>3</sub> was doped from the gas phase" I don't agree. Depending on exposure times, even gas-doped ice films will have substantial "bulk" HNO<sub>3</sub>, most likely in grain boundaries.

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