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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitric acid partitioning in cirrus clouds: a synopsis based on field, laboratory and model studies" *by* M. Krämer et al.

Anonymous Referee #2

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This manuscript by Kramer et al. presents interesting results concerning the partitioning of nitric acid between the gas, particle, and ice phases in the environment of cirrus clouds. As the authors noted, a significant number of field, laboratory, and modeling studies have investigated the HNO3/ice interaction in cirrus clouds, and no strong consensus of HNO3 adsorption on cirrus cloud ice particles has emerged. Understanding the cirrus/HNO3 interaction will be very helpful in understanding the chemistry of nitrogen oxides in the troposphere (and associated tropospheric photochemistry).

Although this manuscript contains some very important results and observations, it tends to lose its focus (the observations are very interesting and are sufficient for a paper in and of themselves) and veers uncontrollably into an unsupported and incomplete theory of HNO3 partitioning in cirrus clouds. The subject area is incredibly complex (due to the noted variables of temperature, ice surface area, HNO3 partial pressure,

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aerosol characteristics, etc.), and the noble but incomplete attempts to describe previous studies confuse readers of this manuscript. I also question how representative the POLSTAR data is of typical cirrus cloud conditions. Therefore, I do not recommend publication at this time.

Despite my strong objections to the unsupported, new "view" of HNO3 in cirrus, the Kramer et al. manuscript is the first one to consider the presence/effect of ammonia on interstitial particles. The authors make an excellent point that aerosol particles within the cloud may need to be incorporated into the partitioning of HNO3. Most previous studies (Meillinger excepted) simply examine gas vs. ice... and the amount within particles needs to be further explored. The manuscript has great promise if it describes the POLSTAR'98 results more thoroughly (with the aerosol and ammonia cases for uptake), and greatly shortens the comparison to others work (it is important to compare and discuss some, but not make it a focus of the manuscript). Their data/analysis on the ice/HNO3 events in POLSTAR are very interesting and should be written up for publication - it would certainly help the atmospheric chemistry community to have another excellent case study of ice/HNO3.

Detailed comments: 1. In the abstract and elsewhere (e.g. first paragraph of introduction, "...up to now..."), I'm not sure that a general picture of the partitioning of HNO3 has emerged (detailed points described later) after reading the manuscript. I recommend staying away from trying to make a grand hypothesis or theory (the data presented doesn't support it), and instead focus on the very interesting field results/interpretation.

2. The POLSTAR data does not seem representative of most tropospheric cirrus clouds - the data seems more stratospheric than tropospheric in nature. The authors even allude to this in the abstract where they mention "more frequently occurring" warm cirrus clouds. To help the readers' understand how representative their data is for cirrus clouds, it would be helpful to quantify this statement. From the data in Table 3, POLSTAR'97 had temperatures of 196 K (HNO3 is very low due to uptake into ternary H2SO4/HNO3/H2O solutions as noted by the authors). It is certainly possible to

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reach these temperatures in the tropical tropopause under some conditions, but rarely ever obtained in the temperate/polar regions. This cloud environment could be argued to be more stratospheric than tropospheric... at any rate, certainly not typical of the troposphere. For POLSTAR'98, locations around events I and II have a temperature of ˜200 K (Table 3) and a nitric acid mixing ratio of 500-600 pptv (Fig. 1) - these conditions again seem more stratospheric than tropospheric. What do other chemical tracers show around events I and II? Again, the cloud could possibly be in the tropopause, but it is not very representative of tropospheric cirrus clouds.

3. Field experiments, introduction section: "Hudson et al. provide the missing parameter..." What parameter was provided to reanalyze Weinheimer et al.?

4. Sec. 2.1.1: No evidence (figures, discussion) is given on the enhancement factors for the inlet. Large uncertainties seem to exist, as shown by the large change between the two experiments. More details supporting the enhancement factors are neededĚhow was the modeling conducted? What was the grid size? A figure would be helpful. How does the uncertainty propogate into errors in all the HNO3 levels (gas phase, ice, particle)? What is 80% uncertainty in the HNO3 measurement... +/- 40% or... +/- 80%? Again, state the results of the error propagation.

5. Sec. 2.1.2: The argument for the small error in the HNO3(gas) measurement is not very strong. From what I read, the authors state that if particulate/ice HNO3 desorbed and inflated the HNO3 gas measurement, flying through an ice cloud would show this. They show in Fig. 1 that HNO3(gas) does not increase while flying through a cloud, therefore, the gas phase HNO3 instrument doesn't sample ice/particle HNO3. The counterargument would be saying that total HNO3 (gas+ice+particle) is relatively constant in and near the cloud, and inside a cloud more HNO3 goes into the condensed phases, so gas phase levels should drop. A constant measurement in and outside a cloud, for these conditions, could indeed be indicative of sampling particle/ice HNO3. More discussion of this point is needed, and a paragraph describing the design of the HNO3 inlet would be helpful (temperature, size, flow rates, composition, etc.).

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6. Sec. 2.1.4: Table 5 should be Tables I and II, respectively. Please show the measured particle size spectra and the associated fit. The readers have no idea of the "appropriateness" of the fit without seeing the actual data. Quantify the uncertainty of the fit versus the overall error in deduced parameters (i.e. how does the supposed +/- 2 uncertainty affect the values in Table 3).

7. Sec. 2.2: The numerous particle mass spec. measurements show that although HNO3/H2SO4/H2O are important aerosol components, significant minerals/dust, carbonaceous, and metal components exist in upper tropospheric aerosol. All of these may impact the validity of even the NH3/H2SO4/HNO3/H2O solution model. Why not use this model instead of the ternary solution, given that the clouds are supposed to be in the troposphere? What does the NH3/H2SO4/HNO3/H2O model suggest for HNO3 uptake at T $<$ 205 K in the presence of ammonia, absence of ammonia? Was the presence of ammoniated salts included/excluded in the model?

8. Sec. 3.1: More details are needed on the general conditions of POLSTAR'98. Temperature, altitude, pressure, potential vorticity, chemical tracers/species in/near the cirrus events are needed - I'm not convinced these clouds are really tropospheric cirrus clouds. The particle spectra are not shown in Figure 1 - rather, the fits are shown - please also show the raw data. Meteorologists would strongly disagree with the statement that the cold cirrus - near 200 K - are typical in the northern wintertime. Present evidence/cite references if true.

9. Sec. 3.1: The fact that HNO3(gas) equilibrated with the amount on the ice and with the particles does not suggest there is no competition between interstitial and ice particles, nor does it suggest that they are independent of one another. For example, consider the case of a given volume of air with a given volume of HNO3 all in the gas phase. Suppose HNO3 is taken up by the particles, the gas phase level must decrease (conservation of HNO3 molecules) to achieve a new equilibrium. If an ice particle then forms and HNO3(gas) goes onto ice, the gas phase level will be depleted even further. The gas phase will decrease to some level in equilibrium with both the

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particles and the ice. I don't take issue with the assumption of equilibrium (without it, the already complex analysis would become even more complex), but please clarify your statements.

10. Sec. 3.2: A distinction between film and particle studies is made, but no justification is given as to why particle studies are more appropriate than film studies. All of the experimental results (film and particle) to date are at least somewhat frought with uncertainties and problems (e.g., not knowing partial pressures, not knowing surface areas, etc.). Why is a model study included (which is based partly on film studies and on another model study)? The POLSTAR results should be compared to SUCCESS and other ice/HNO3 experimental results (field and laboratory). Why is a model study (which itself is based off lab and another model study) included here? It seems like data is being selectively used to fit the authors' general hypothesis, and no justification is given to exclude other studies. This is a major problem with the manuscript. Finally, the last sentence on "competition", please clarify based on comment (9) above.

11. Section 3.3: There are still no labels on Figure 2. Either label it as appropriate or remove it. I'm guessing for HNO3_ptcl and HNO3_ice, the scale is 0-100% (i.e. the partitioning). What are the units for ice surface and H2O? Very confusing. No inclusion of ammonia is noted in this figure... and ammonia would certainly change these results. The general statement in the last paragraph is only true based upon the stratospheric model (H2SO4/H2O/HNO3) results, and the actual data from various field and laboratory studies are more ambiguous.

12. Section 4: Apples and oranges are being compared, and the discussions are incomplete and confusing. I recommend saving this section for a separate manuscript to give appropriate time, space, and discussion to all the published works. For example, at least five variables are being compared: temperature, ice surface area density, partial pressure of HNO3, surface coverage, and composition of the interstitial aerosol particles. Although some of the variables may be related (e.g. colder temperatures, more HNO3 in particle phase), the various studies presented in Figure 4 (an inclusive

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list this time around, despite the distinction made earlier in the manuscript about films and particle experiments) all had much different conditions (some of which didn't follow the general rules noted in section 3.3). To reduce them to one variable, e.g. partial pressure, is incomplete without a more detailed/qualitative discussion of why/how certain data points are above/below the model fits. A number of reasonable explanations can explain why certain results do/do not fit the model data. Furthermore, model data make great simplications, too. A detailed discussion of the surface adsorption models (Langmuir, FFH, etc.), Gibbs free energies of adsorption, and the differences between particle and film experiments is beyond the scope of this manuscript (each could be and has been a paper in its own right). For example, Sec. 4.2.3: the phrases "...we suspect that the amount of adsorption free energy could be lower for ice particles at lower temperatures. A possible explanation may be that the strength of the hydrogen bonds and/or the ice surface structure depends on temperature" is highly speculative, is not supported by any data or references, and is not appropriate for the manuscript.

13. Sec. 5: If "it is not possible to derive a general picture on the mechanisms of HNO3 uptake" on ice from analyzing the various field and laboratory data, how can the authors state that a new hypothesis has been made in this manuscript?

14. Units in Table I for the particle probes should be in mm instead of nm.

OVERALL COMMENT:

The authors should certainly compare their data to the various field and laboratory studies, but the focus of the manuscript should be on their data, as opposed to lengthy but largely unprofound comments upon surface chemistry, thermodynamics, surface models, and experimental differences between techniques. Even with the data presented in the manuscript, I don't understand or see their "new hypothesis" of HNO3/cirrus clouds. No data presented supports a general view of HNO3/cirrus.

The strength of this manuscript is in the authors' own data (and it is very nice data) - the two nice ice/HNO3 events of POLSTAR'98 and reanalysis of the first POLSTAR.

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Although a more detailed discussion is needed here, and a more convincing case of its relevance to cirrus clouds needs to be made, the field data and analysis of their data is definitely publishable and very interesting. The authors also make a very important point that interstitial aerosols need to be considered for HNO3 within cirrus clouds.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 413, 2003.