

## ***Interactive comment on “The adsorption of peroxyntic acid on ice between 230 K and 253 K” by T. Ulrich et al.***

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We thank S. le Calve for the useful comments and for the detailed list of questions and suggested corrections. We apologize for the extra time and effort that might have been needed to evaluate the manuscript due to the sometime confusing use of the English language. We took the opportunity to edit the language and structure of the whole manuscript. The revised version was additionally restructured, rewritten, and shortened throughout the manuscript. In the following the comments and questions of the reviewer are answered.

Minor corrections:

C14606

1 – Page C12944, Lines 8-9: “Page 26817, line 4 : “Deposition to snow has been proposed as such sink” should be replace by “Deposition to snow has been proposed as such a sink”.

Response: Done.

2 – Page C12945, Lines1-2: “Page 26817, line 1 : “which generally overestimate its gas-phase concentrations”. Please add references about models or previous works.”

Response: Done. We have restructured the manuscript as follows:

The fate of HO<sub>2</sub>NO<sub>2</sub> in the atmosphere is not well enough known to be captured in atmospheric-chemistry models, which generally overestimate its gas-phase concentration (Slusher et al., 2002; Kim et al., 2007). Diurnal profiles of HO<sub>2</sub>NO<sub>2</sub>, observed at South Pole, could only be reproduced when deposition to snow was postulated as sink (Slusher et al., 2002). In the upper troposphere a HO<sub>2</sub>NO<sub>2</sub> sink is also missing from the model descriptions. Currently the observed altitude profiles cannot be reproduced (Kim et al., 2007). The authors suggested uptake to ice particles in cirrus clouds as one of several potential sink processes.

3 - Page C12945, Lines 3-5: “Page 26817, lines 4-5 : “the observed decrease in gas-phase HO<sub>x</sub> concentration at high NO<sub>x</sub> levels”. Please, indicate that high concentrations of NO<sub>x</sub> favor the formation of HO<sub>2</sub>NO<sub>2</sub>.”

Response: We thank the author for the useful suggestion. We have rewritten the section as follows:

Due to the thermal equilibrium of HO<sub>2</sub>NO<sub>2</sub> with HO<sub>2</sub> and NO<sub>2</sub> (Gierczak et al., 2005), HO<sub>2</sub>NO<sub>2</sub> makes up a significant fraction of the total nitrogen oxide budget mainly in the colder parts of the environment. For example, field measurements have shown gas phase concentrations of up to  $3 \times 10^{10}$  molecules cm<sup>-3</sup> in Antarctica (Slusher et al., 2002; Slusher et al., 2010) and  $6 \times 10^8$  molecules cm<sup>-3</sup> in the upper troposphere (Kim et al., 2007). Field data further indicate a strong chemical coupling of HO<sub>2</sub>NO<sub>2</sub> and NO

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(Davis et al., 2008; Slusher et al., 2010) and formation and deposition of HO<sub>2</sub>NO<sub>2</sub> has been suggested to contribute to the reduction of OH at increasing NO levels (Grannas et al., 2007).

4 - Page C12945, Lines 6-8: "Page 26817, lines 15-17: "The uptake coefficient is defined as the net probability that a molecule that gas-kinetically collides with a surface is taken up at the surface." I wonder if this sentence is really useful."

Response: We agree. In fact, the manuscript can be further improved by omitting the discussion on the uptake coefficient. We now emphasize the strong uptake observed by Li without discussing the uptake coefficient:

The choice to include a strong deposition of HO<sub>2</sub>NO<sub>2</sub> to the snow or ice clouds is generally motivated by an earlier laboratory study that showed a significant uptake of HO<sub>2</sub>NO<sub>2</sub> to ice surfaces persisting over longer times (Li et al., 1996).

5 - Page C12945, Lines 9-10: "Page 26817, lines 23-24 : Please explain the sentence "the work was certainly done outside the ice stability regime of the HNO<sub>3</sub> –water phase diagram.""

Response: The main point is that Li et al exposed the ice film to high concentrations of HO<sub>2</sub>NO<sub>2</sub> and of HNO<sub>3</sub> (which is a by-product of the HO<sub>2</sub>NO<sub>2</sub> synthesis). At such high concentrations (and low temperatures) HNO<sub>3</sub> forms hydrates, and ice is no longer the thermodynamically stable phase. A similar argumentation is likely for HO<sub>2</sub>NO<sub>2</sub> even though the water – HO<sub>2</sub>NO<sub>2</sub> phase diagram is not known. The formation of hydrates is critical, because this leads to a totally different uptake behavior of trace gases to the surface. We hope the revised version makes this point clearer:

This result can however not be applied to atmosphere – ice interactions at environmental conditions for two reasons. First, the HO<sub>2</sub>NO<sub>2</sub> concentration during the uptake experiments was up to  $2 \times 10^{13}$  molecules cm<sup>-3</sup>. Such high levels of acidic trace gases may induce formation of hydrates significantly alter the interaction of trace gases

C14608

with the surface (Ullerstam et al., 2005; Huthwelker et al., 2006). Secondly, Li et al. (1996) identified HNO<sub>3</sub> as major nitrogen oxide contamination in the gas-phase with levels of up to 9 % of HO<sub>2</sub>NO<sub>2</sub>, which corresponds to concentrations of up to  $2 \times 10^{12}$  molecules cm<sup>-3</sup>. In literally all of their experiments, Li et al. (1996) probed the interaction of HO<sub>2</sub>NO<sub>2</sub> with nitric acid hydrates and not with water ice, which is not stable at such high HNO<sub>3</sub> levels (Thibert and Dominé, 1998).

6 - Page C12945, Lines 11-12: "please Page 26818, lines 22-23 : "NO<sub>2</sub> at typically  $3.4 \cdot 10^{12}$  molecules cm<sup>-3</sup> initial concentration" please indicate how you quantify NO<sub>2</sub> concentrations."

Response: We quantified NO and NO<sub>2</sub> only prior to the addition of CO, because CO interfered with the NO measurement. In those experiments NO was near the detection limit of the NO<sub>x</sub> analyzer at around  $2 \cdot 10^9$  molecules cm<sup>-3</sup>. We regret that this slipped our attention and that we discussed NO<sub>2</sub> in the manuscript, when it might have been a mixture of NO and NO<sub>2</sub>. This does, however, not change the results or the argumentation, as both NO and NO<sub>2</sub> do not interfere with the adsorption experiments of HO<sub>2</sub>NO<sub>2</sub>. We corrected this throughout the manuscript.

7 - Page C12945, Line 13-15: Page 26819, lines 1-2 : "of the by-products HONO, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> in the gas flow was reduced by a Ti(IV) oxysulfate denuder and by a cooling trap at 243 K" Can you explain why this denuder permits to remove some impurities?"

Response: The Ti-denuder and the cooling trap had been described in the Methods and in the Result and Discussion section. To make the revised manuscript easier to follow, we limit the discussion of the denuders in the Methods section to a description of how the denuders are prepared. A detailed discussion on their performance and on their operation principles follows in the Results and Discussion part. The Ti-denuder traps H<sub>2</sub>O<sub>2</sub> because Ti-H<sub>2</sub>O<sub>2</sub> complexes are formed. This technique was used earlier by Possanzini et al. (1988) to quantify H<sub>2</sub>O<sub>2</sub>. The denuder is however not very

C14609

selective, as also HO<sub>2</sub>NO<sub>2</sub> and HNO<sub>2</sub> are removed from the gas phase

The Methods section now reads: After the synthesis the gas flow was cleaned from by-products using a Ti(IV) oxysulfate denuder and a cooling trap at 243 K (see Results and Discussion).

And the Results and Discussion section has been modified as follows: Figure 2 shows the performance of the two purification steps for a typical experimental run: Concentrations of the trace gases with time are given when they passed both the Ti(IV) denuder and the cooling trap (235-265 min), only the Ti(IV) denuder (265-295 min), and neither of the two (295-330 min). We found that the Ti(IV) denuder alone removes 96% of the H<sub>2</sub>O<sub>2</sub> (Fig. 2, 265 - 295 min and 295 - 330 min). Ti(VI) oxysulphate forms [Ti(O<sub>2</sub>)(OH)<sub>aq</sub>]<sup>+</sup> complexes with H<sub>2</sub>O<sub>2</sub>. This has previously been used as an analytical method (Possanzini et al., 1988). Also HONO was reduced by 94 % and 55 % of the HO<sub>2</sub>NO<sub>2</sub> is trapped by the denuder, which lowers the overall yield of the synthesis route substantially. NO<sub>x</sub> and HNO<sub>3</sub> are increased by 15 % and 240 % when the Ti(IV) denuder is used. This indicates that these species were produced by redox processes in the Ti(IV) denuder system. The subsequently installed cooling trap reduces the HNO<sub>3</sub> concentration by 86 % and the H<sub>2</sub>O<sub>2</sub> concentration by 63 % of their respective concentration after the Ti(IV) denuder (Fig. 2, 235 - 267 min).

8 - Page C12945, Lines 16-19: "Page 26819, lines 22-23 : "in most experiments a slight loss of 15% (mean value) was observed". Does it mean that water vapor was not added to the main nitrogen flow to provide the exact partial pressure of water equal to the vapor pressure of water over the ice film?"

Response: The nitrogen flow was always humidified to match the vapor pressure over the ice in the CWFT. The observed loss in weight was presumably an artifact. First, the humidifier that consists of a precisely tempered ice surface over which a flow of nitrogen is lead is very precise. Additionally, we ensured that the gas flow entering the CWFT and the vapor pressure over the ice in the CWFT were identical using the CIMS.

C14610

The revised section reads:

To ensure water vapor equilibrium of the gas and the ice phase, the relative humidity in the gas flow was set to match the vapor pressure of the ice in the CWFT. This was done by adding 1500 ml min<sup>-1</sup> N<sub>2</sub> that had passed a humidifier.

9 – Page C12945, Line 20: "Page 26819, line 23: replace "weighing" by "weighting" (2 times)".

Response: We kindly disagree here. We checked the correct spelling in the US /British dictionary: weighing is corret.

10 - Page C12945, Lines21-25: "Page 26819, line 29: "containing around 8.16\_1010 molecules cm<sup>-3</sup> HO<sub>2</sub>NO<sub>2</sub>". This indicates that the authors work always with the same concentration HO<sub>2</sub>NO<sub>2</sub>. Did they try to change this concentration to plot the surface concentration versus the gas phase concentration in order to check that they were in the linear part of the isotherm. This work should be carried out for at least one or two temperatures."

Response: It is true that we did not record a concentration dependency of the adsorption and we state this more clearly in the revised version. We think that the surface coverage of HO<sub>2</sub>NO<sub>2</sub> (5 % at max.) is low enough to be in the linear adsorption range. The revised section reads:

The concentration of HO<sub>2</sub>NO<sub>2</sub> in the CWFT was kept constant for all experiments.

Surface coverage is at most a few percent of a monolayer, as estimated with a maximal monolayer capacity of 3×10<sup>14</sup> molecules cm<sup>-2</sup> found for HON O and HNO<sub>3</sub> (Crowley et al., 2010). Adsorption at such a low surface coverage is most likely in the linear adsorption range of the Langmuir adsorption isotherm.

11 - Page C12946, Lines 1-5: "Page 26820, lines 27-29 : "Stable humidity during the experiment, and in particular identical humidity in the carrier gas, whether or not it passed the ice in the CWFT," How the authors change the partial pressure of water

C14611

over the ice film when temperature changes ? Is this partial pressure equal to the exact vapor pressure of water over the ice film at the given temperature”

Response: The temperature of the humidifier was set so the humidity in the gas flow entering the CWFT matched the vapor pressure of the ice in the CWFT, as detailed above. Then the relative humidity in the gas flow before and after the CWFT was measured using the CIMS. This measurement typically revealed a small mismatch of the humidity. The temperature in the CWFT, and thus the vapor pressure over the ice sample, was then adapted.

12 – “Page 26823, eq. R5 and R6: To avoid these two reactions, CO can be used as scavenger as mentioned by the authors. Here, it could be useful to calculate the relative rate of the reactions (R5/R3 and R6/R3) using the rate coefficients and typical concentrations measured in the experiments.”

Response: We agree, thank you for this suggestion. The concentration of CO ( $10E16$  molec/cm<sup>3</sup>) exceeds typical NO and NO<sub>2</sub> levels ( $<10E13$  molec/cm<sup>3</sup>) and the ratio of the rate constants R5/R3 is 0.06 and the ratio of R6/R3 is 0.03. This shows that the scavenging of OH by CO is much faster than the reaction of OH with NO and NO<sub>2</sub>. The revised section reads:

The low levels of by-products are supported by a comparison of the rate constants showing that OH is scavenged by CO much faster than its reaction with either NO or NO<sub>2</sub>. The ratios of rate constants of R5/R3 and R6/R3 are 0.06 and 0.03 respectively (Atkinson et al., 2004) and the CO concentration exceeds those of NO and NO<sub>2</sub> by three orders of magnitude.

13 - Page C12946, Lines 10-11: “Page 26823, line 25: On the figure 2, I did not see any increase of NO<sub>2</sub>. Do you mean H<sub>2</sub>O<sub>2</sub> or NO<sub>2</sub> ?”

Response: We agree that the description of the figure was confusing. Both NO<sub>2</sub> and HNO<sub>3</sub> concentrations are higher when the gas flow passed the denuder (265-295 min)

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compared to their concentration in the gas flow when the denuder is bypassed (295 min -330 min). The description of the figure is revised as follows:

Figure 2 shows the performance of the two purification steps for a typical experimental run: Concentrations of the trace gases with time are given when the gas flow passed both the Ti(IV) denuder and the cooling trap (235-265 min), only the Ti(IV) denuder (265-295 min), and neither of the two (295-330 min). . . . NO<sub>x</sub> and HNO<sub>3</sub> are increased by 15 % and 240 % when the Ti(IV) denuder is used. This indicates that these species were produced by redox processes in the Ti(IV) denuder system. The subsequently installed cooling trap reduces the HNO<sub>3</sub> concentration by 86 % and the H<sub>2</sub>O<sub>2</sub> concentration by 63 % of their respective concentration after the Ti(IV) denuder (Fig. 2, 235 - 265 min).

14 - Page C12946, Lines 12-13: “Page 26824, line 28: “Reasons for this might be the increased flow velocity through the photo reactor”. Why will the increase of flow velocity increase the yields of impurities such as HNO<sub>3</sub> and HONO ?”

Response: We agree that the sentence is unclear. We think the main reason for the different yields is the much more selective mode of detection for HNO<sub>3</sub> and HONO in this study. The section is edited as follows:

The reason for this might be a more selective and direct detection mode of HNO<sub>3</sub> and HONO. In the previous study both species were only indirectly determined.

15 - Page C129, Lines 15-16: “Page 26825, line 5 : “and its intensity drops to the background level.” Can you give the ice surfaces exposed to gas pollutant ?”

Response: We will add this information. The surface area is 110.6 cm<sup>2</sup>.

16 - Page C129, Lines 16-17: “Page 26825, line 25: “thus at most a few percent of a monolayer.” How do you estimate the monolayer capacity for HO<sub>2</sub>NO<sub>2</sub> ?”

Response: We agree that a citation and explanation is missing here, and added it. We used the monolayer capacity for HONO and HNO<sub>3</sub> as recommended by Crowley et al.

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2010.

17 - Page C12946, Lines 19-26: "Page 26825, lines 19-20: "acetic acid (Kerbrat et al., 2010a; Symington et al., 2010; von Hessberg et al., 2008), The following publication has been published first and should be cited : o S. Picaud, P. Hoang, N. Peybernès, S. Le Calvé, P. Mirabel, Adsorption of acetic acid on ice. Experiments and molecular dynamics simulations, J. Chem. Phys., 122, 194707-1, 2005. - Page 26826, line 10 : For acetone, the authors prefer to cite their publications although they are many others publications related to reversible adsorption of acetone (for example Winkler et al., Peybernès et al.)."

Response: Thank you, we have added the references. In the revised section the text has been modified and restructured:

Weaker acids, such as HO<sub>2</sub>NO<sub>2</sub>, show a fast and complete recovery. Analogous examples are formic acid (von Hessberg et al., 2008; Symington et al., 2010), acetic acid (Picaud et al., 2005; von Hessberg et al., 2008; Kerbrat et al., 2010a; Symington et al., 2010), HONO (Chu et al., 2000), and SO<sub>2</sub> (Clegg and Abbatt, 2001).

The observation of reversible adsorption is in agreement with other data available for weak acids or non-acidic species such as H<sub>2</sub>O<sub>2</sub> (Pouvesle et al., 2010), acetone (Winkler et al., 2002; Peybernès et al., 2004; Bartels-Rausch et al., 2005), formic acid (von Hessberg et al., 2008) and acetic acid (Sokolov and Abbatt, 2002; Symington et al., 2010).

18 - Page C12947, Lines 1-7: "Page 26827, lines 12-13 : "For the strong acids HNO<sub>3</sub> (Ullerstam et al., 2005) and HCl (McNeill et al., 2006) the peak area was significantly lower in the desorption experiments." This sentence could be completed as follows : " : : desorption experiments showing that the adsorption was not reversible for these strong acids". - Page 26827, line 16: "at temperatures below 240 K". Please modify as follows : "at temperatures ranging from 230 and 240 K" - Page 26827, Eq. 2: nads is not defined."

C14614

Response: We thank the author for the useful suggestions. "nads" is the numbers of molecules adsorbed on the ice surface [molecules].

19 - Page C12947, Lines 8-9: "Page 26828, line 7 : "KLinC at 230 K is 91.2 ± 15.7 cm and decreases to 6.0 ± 0.4 cm at 253 K." Can you indicate what the uncertainties represent?"

Response: We agree that the meaning of the error and how it was derived is unclear. We used the 95 % confidence interval of the linear fit in Figure 4 to derive uncertainty. Based on this interval, the standard deviation of the individual is calculated. In the revised manuscript we restructured those sections and added a paragraph for the discussion of the uncertainty:

All uncertainties given as 95 % confidence intervals

Uncertainties The uncertainty of nads, KLinC, the exponent of the Arrhenius temperature dependency and the  $\Delta H_{0ads}$  was determined by the 95 % confidence interval of the fit through 22 data points. The reported error represents random variations between individual experiments and is expressed as 2 times the standard deviation in each direction. The 95 % confidence interval of the fit agreed well with the confidence interval of 5 repeated experiments at 230 K. A rough estimation of the individual contributions to the total uncertainty revealed that fluctuations in nads, which are 19 % of the mean value and instrumental fluctuations, which are 5 % of the mean value, contribute to an half of the total uncertainty of nads. Other random fluctuations like the temperature of the CWFT or the fluctuations of the flow through the CWFT have a lower impact on the error. Co-adsorption has been identified as a possible systematic error for the analysis of the breakthrough curves and the determination of KLinC of HO<sub>2</sub>NO<sub>2</sub>. The estimation of the effect of co-adsorption relies on parameters that had to be assumed, which might have an uncertainty by themselves. An error in nmax of H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>NO<sub>2</sub> was found to be negligible. In the interval of nmax from  $2 \times 10^{14}$  molecules cm<sup>-2</sup> to  $4 \times 10^{14}$  molecules cm<sup>-2</sup>, KLinC only changed by 7.4 % at 230 K. The gas

C14615

phase concentration of H<sub>2</sub>O<sub>2</sub>, which was tested in the  $\pm 50\%$  interval, changed K<sub>LinC</sub> by 7% at 230 K. This deviation is also within the experimental scatter. A change in K<sub>LinC</sub> of H<sub>2</sub>O<sub>2</sub> within a  $+150\% - 66\%$  interval, leads to a change in K<sub>LinC</sub> of 22%. This effect was the greatest, but still inside the bounds of error of experimental scatter. In summary the estimation of the parameters is robust, and the conclusion, that co-adsorption is negligible, is valid.

20 - Page C12947, Lines 10-12: "Page 26828, line 13: "their uncertainty are independent the concentration of HO<sub>2</sub>NO<sub>2</sub>" This sentence should be corrected as follows : "their uncertainty are independent of the concentration of HO<sub>2</sub>NO<sub>2</sub>"

Response: Done.

21 - Page C12947, Lines13-15: "Page 26829, Eq. 3: Knowing their pK<sub>a</sub> and their H<sub>2</sub>SO<sub>4</sub>, could we apply this equation for acidic species never studied (on ice) so far ? Are there species of atmospheric interest ?"

Response: This is correct, but we think it is beyond the scope of this article to estimate the partition coefficient for species not studied yet. An interesting species could be methane sulfonic acid since it is involved in aerosol formation above sea water. The revised section reads:

The relationship found is given in Eq. (4) and can be used to roughly estimate the partitioning of any acidic trace gas to ice.

22 - Page C12947, Lines 16-18: "Page 26830, line 13 : "except from a very high enthalpy of adsorption for HNO<sub>3</sub>" I suggest to modify as follows : " except if one consider the very high enthalpy of adsorption for HNO<sub>3</sub>: : :".

Response: Done.

23 - Page C12947, Lines 19-24: "Page 26831, lines 8-13: "HNO<sub>3</sub> completely adsorbs within less than 2 cm of the flow tube at any temperature and its influence on the partitioning of HO<sub>2</sub>NO<sub>2</sub> to the ice in equilibrium 10 over the whole length of the CWFT

C14616

is thus neglected. H<sub>2</sub>O<sub>2</sub> adsorbs along a length of up to 30cm with a surface coverage ranging from 5% to 10% for temperatures between 253 K and 238 K, and from 10% to 18% below 238 K." The authors should detail the calculation made for length for both HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>."

Response: We agree. To calculate the length, the surface concentration of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> was derived following Eq. 2 with K<sub>LinC</sub> taken from Crowley et al. 2010 and Pouvesle et al. 2011 and with the measured gas phase concentration. The area respectively the length is then calculated from the surface concentration with the flux of the respective molecules into the CWFT. The revised section reads:

To estimate the impact of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> on HO<sub>2</sub>NO<sub>2</sub> adsorption, the length on which they are present in the CWFT was derived. For this the surface coverage (Eq. 2) was calculated with K<sub>LinC</sub> taken from Crowley et al. (2010) and Pouvesle et al. (2011) and with the measured gas phase concentration. The total area, i.e. the length, in the column where both species adsorb is then derived based on the total flux of molecules into the CWFT during the experiment and the surface coverage.

24 - Page C12947, Lines25-26: "Page 26831, line 18: "This reduced uptake slightly reduces the : : " : reduce is used 2 times in the same sentence."

Response: We thank the author for the useful suggestion.

25 - Page C12948, Lines1-4: "Page 26831, lines 19-20 : "As this effect is well within the experimental uncertainty of K<sub>LinC</sub>, we neglected the influence of competitive adsorption." This competitive adsorption should be taking account for the estimation of uncertainties. This contributes to increase the uncertainties."

Response: Because the effect of co-adsorption is a systematic error, we prefer to discuss it independently of the (random) standard deviation. To give an impression how much the values would be shifted, we give the prediction interval for K<sub>LinC</sub> based on competitive adsorption in figure 4. The revised text reads:

C14617

To quantify the possible influence of H<sub>2</sub>O<sub>2</sub> on the adsorption of HO<sub>2</sub>NO<sub>2</sub>, we used the competitive Langmuir model as detailed in (Kerbrat et al., 2010a). The model showed that K<sub>LinC</sub> is reduced by 20 % at 230 K, by 8 % at 238 K and by 5 % at 250 K. This is thus a potential systematic error of our results at low temperatures. However, as the deviation is well within the experimental scatter of K<sub>LinC</sub>, we neglected the influence of competitive adsorption (Fig. 4).

See Fig. 1.

Figure 4. Natural logarithm of K<sub>LinC</sub> versus the inverse temperature for HO<sub>2</sub>NO<sub>2</sub> (blue diamonds). When several data points were available mean values are plotted with an uncertainty of two times the standard deviation. The blue, dotted lines give the 95 % confidence bounds for the linear fit (blue solid line). The thick blue dots give the maximum error with included competitive adsorption. The blue crosses indicate desorption experiments. The data are compared to the IUPAC recommendation (Crowley et al., 2010) for HONO (green, dashed line with triangles) and HNO<sub>3</sub> (red, dash-dotted line with squares). The dotted lines show the error for HONO and HNO<sub>3</sub> according to the IUPAC recommendation.

26 - Page C12948, Lines5-8: "Page 26832, line 16: modify as follows : "gaseous HO<sub>2</sub>NO<sub>2</sub> would be detected" - Page 26834, lines 11-13: "Acidity and solubility of the trace gas could be shown to have an important impact on the adsorption behavior." Please mention that is only true for acidic species."

Response: We thank the author for the useful suggestion. The manuscript was new structured, edited and shortened. The text reads now:

The good correlation illustrates the importance of both the acidity and the solubility on the partitioning to ice. Apparently similar molecular properties determine the tendency for uptake into water and the adsorption on ice for these acidic trace gases. This even holds for acidic organic trace gases.

C14618

27 - Page C12948, Line 9: "Page 26842, Fig 1 : This figure is complicated and not very understandable."

Response: We agree with this statement, the figure was enhanced:

See Fig. 2.

Figure 1. Experimental setup consisting of a gas-phase synthesis, a purification step, the adsorption experiments (CWFT), and the detection step.

28 - Page C12948, Lines10-14: "Page 26847, Fig 6: Note that the experiments have been performed between 230 and 250 K for HO<sub>2</sub>NO<sub>2</sub> although the authors derive fraction down to 200 K ! This should be justified. Note also that when you used data calculated at 200 K from experimental data obtained at 230 K, the resulting uncertainties are high so that the conclusions are uncertain."

Response: We agree with this statement, but would argue that extrapolating our data should be valid, because of the good linear fit in Figure 4. The text was newly structured and edited:

The temperature range for the experiments presented in this work ranges from 230 K to 253 K. Data is extrapolated to temperatures down to 200 K in Fig. 6 which potentially adds uncertainty. Taken the excellent linear fit of ln(K<sub>LinC</sub>) to 1/T that represents our data, we suggest that this extrapolation is reasonable for a rough estimate of the partitioning of HO<sub>2</sub>NO<sub>2</sub> to ice in the upper troposphere.

29 - Page C12948, Lines 15-17: "Page 26847, Fig 6, legend: please mention that the fraction are calculated according to eq. (4). Please add the references for the data used (Crowley et al for HNO<sub>3</sub> and this work for HO<sub>2</sub>NO<sub>2</sub>)."

Response: We agree with this statement, the references should be included. The edited caption reads:

Figure 6. Fraction of adsorbed HO<sub>2</sub>NO<sub>2</sub> (blue line) and HNO<sub>3</sub> (red line, triangles) to

C14619

cirrus clouds at temperatures of the upper troposphere. Solid lines represent clouds with a surface area density of  $10^{-5} \text{ cm}^{-1}$ , dashed lines represent clouds with a surface area density of  $3 \times 10^{-4} \text{ cm}^{-1}$ . Data for  $\text{HNO}_3$  was taken from the IUPAC recommendations (Crowley et al.), the data for  $\text{HO}_2\text{NO}_2$  is from this work.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 26815, 2011.

C14620

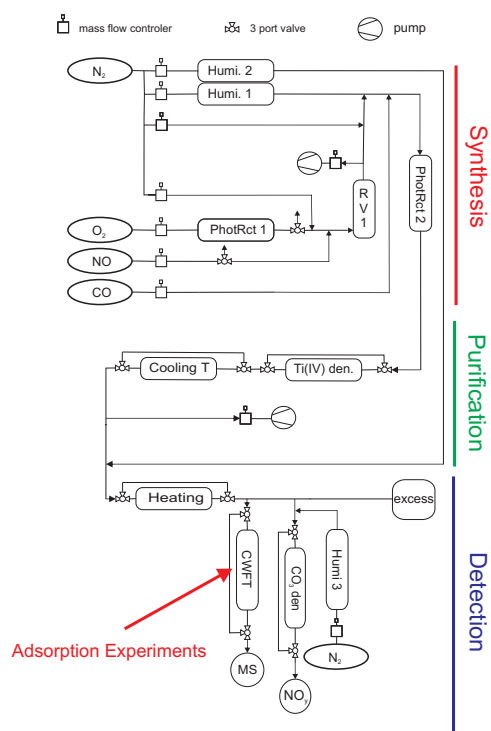


Fig. 1.

C14621



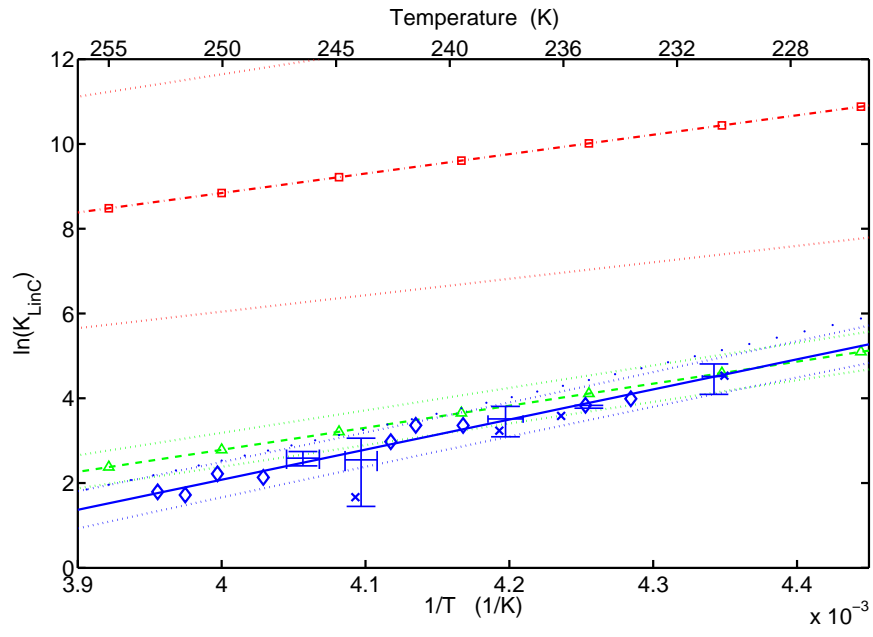


Fig. 2.

C14622