

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

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General comment :

This publication is of great scientific interest. The original synthesis of HO₂NO₂ and precautions that reduce the amount of impurities, is a strong point of this work. Analysis of experimental data was carried out in complete state of the art and the results have some real atmospheric implications. However, some corrections or additional information must make prior to publication.

Minors corrections :

- 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”.

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Discussion Paper



- Page 26817, line 1 : “which generally overestimate its gas-phase concentrations”. Please add references about models or previous works.
- Page 26817, lines 4-5 : “the observed decrease in gas-phase HO_x concentration at high NO_x levels”. Please, indicate that high concentrations of NO_x favor the formation of HO₂NO₂.
- 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.
- Page 26817, lines 23-24 : Please explain the sentence “the work was certainly done outside the ice stability regime of the HNO₃ –water phase diagram.”
- Page 26818, lines 22-23 : “NO₂ at typically 3.4×10^{12} molecules cm⁻³ initial concentration” please indicate how you quantify NO₂ concentrations.
- Page 26819, lines 1-2 : “of the by-products HONO, HNO₃, and H₂O₂ in the gas flow was reduced by a Ti(IV) oxysulfate denuder” Can you explain why this denuder permits to remove some impurities.
- 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 ?
- Page 26819, line 23: replace “weighing” by “weighting” (2 times)
- Page 26819, line 29: “containing around 8.16×10^{10} molecules cm⁻³ HO₂NO₂”. This indicates that the authors work always with the same concentration HO₂NO₂. 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.

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- 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 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
- 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.
- Page 26823, line 25: On the figure 2, I did not see any increase of NO₂. Do you mean H₂O or NO₂ ?
- 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 HNO₃ and HONO ?
- Page 26825, line 5 : “and its intensity drops to the background level.” Can you give the ice surfaces exposed to gas pollutant ?
- Page 26825, line 25: “thus at most a few percent of a monolayer.” How do you estimate the monolayer capacity for HO₂NO₂ ?
- 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.).

- Page 26827, lines 12-13 : “For the strong acids HNO₃ (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.
- Page 26828, line 7 : “K_{LinC} 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 ?
- Page 26828, line 13: “their uncertainty are independent the concentration of HO₂NO₂” This sentence should be corrected as follows : “their uncertainty are independent of the concentration of HO₂NO₂”
- Page 26829, Eq. 3: Knowing their pK_a and their H₂98, could we apply this equation for acidic species never studied (on ice) so far ? Are there species of atmospheric interest ?
- Page 26830, line 13 : “except from a very high enthalpy of adsorption for HNO₃” I suggest to modify as follows : “ except if one consider the very high enthalpy of adsorption for HNO₃. . .”
- Page 26831, lines 8-13: “HNO₃ completely adsorbs within less than 2 cm of the flow tube at any temperature and its influence on the partitioning of HO₂NO₂ to the ice in equilibrium 10 over the whole length of the CWFT is thus neglected. H₂O₂ 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 HNO₃ and H₂O₂.
- Page 26831, line 18: “This reduced uptake slightly reduces the. . .” : reduce is used 2 times in the same sentence.

- Page 26831, lines 19-20 : “As this effect is well within the experimental uncertainty of K_{LinC}, 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.
- Page 26832, line 16: modify as follows : “gaseous HO₂NO₂ 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.
- Page 26842, Fig 1 : This figure is complicated and not very understandable.
- Page 26847, Fig 6: Note that the experiments have been performed between 230 and 250 K for HO₂NO₂ 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.
- 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 HNO₃ and this work for HO₂NO₂).

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