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## Comment on amt-2021-291

Anonymous Referee #2

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Referee comment on "Detection of nitrous acid in the atmospheric simulation chamber SAPHIR using open-path incoherent broadband cavity-enhanced absorption spectroscopy and extractive long-path absorption photometry" by Sophie Dixneuf et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-291-RC1>, 2021

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Dixneuf et al. present new measurements of nitrous acid, nitrogen dioxide and methacrolein at the Jülich SAPHIR chamber by open-path incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS), chemiluminescence spectrometry, long-path absorption photometry (LOPAP) and proton-transfer mass spectrometry (PTR-MS). The measurement of these analytes by these techniques have been described in the literature (i.e., are not novel) but there is nevertheless value in the comparisons and technical details presented.

Overall, the manuscript should be acceptable for publication once the authors have considered and addressed my comments below.

### General comments:

(1) The main focus of this paper is on the HONO intercomparison. There have been several such papers in the literature (e.g., Kleffmann et al., Atmos. Meas. Tech., 14, 5701-5715, 10.5194/amt-14-5701-2021, Rodenas et al., 2013, doi: 10.1007/978-94-007-5034-0\_4 2021; Pinto et al., JGR 119, 5583, 2014, doi: 10.1002/2013JD020287; Wu et al., Atmospheric Environment 95, 544-551, 2014, doi: 10.1016/j.atmosenv.2014.07.016; Crilley et al., Atmos. Meas. Tech., 12, 6449-6463, 10.5194/amt-12-6449-2019, 2019; Yi et al. Atmos. Meas. Tech., 14, 5701-5715, 10.5194/amt-14-5701-2021, 2021). What was learned in this work that confirmed or was new or different from these prior intercomparisons? It seems an entire paragraph of discussion should be added (at least).

(2) The quantification of methacrolein by DOAS and validation vs. PTR-MS is novel (it was news to me, at least) and should be presented in more detail and discussed.

(3) There has been some literature that could aid in the interpretation of some results. For example, Rohrer et al. (ACP 5, 2189, 2005, [www.atmos-chem-phys.org/acp/5/2189/](http://www.atmos-chem-phys.org/acp/5/2189/)) in their Figures 1 and 2 (top left) show LOPAP HONO data larger than calculated HONO concentrations that continued (and in one case drastically increased) "in the dark" which should be mentioned in section 4.2 of this paper. Given this history, perhaps a more critical discussion of LOPAP performance is warranted.

(4) Rohrer et al. (ACP 5, 2189, 2005, [www.atmos-chem-phys.org/acp/5/2189/](http://www.atmos-chem-phys.org/acp/5/2189/)) box-modeled the evolution of HONO mixing ratios. Why was this not done here? This would have been useful for the interpretation of LOPAP and IBBCEAS data, especially when diverge.

(5) Re IBBCEAS data reduction - the background (R measurement) was taken at the beginning of each day. Have the authors considered averaging between consecutive measurements to reduce instrument drift. Some data (e.g., June 10, Figure S8) suggest that drift could be a substantial factor!

Minor comments:

Line 20, abstract: "methacrolein was detected at mixing ratios <5 ppbv" It would be more informative if the LOD for methacrolein was stated (could be combined with the previous sentence) rather than burying this information in Figure S7.

Line 20-22, abstract: Please state what the results of the comparisons were.

Line 57. "sampling lines are known to cause unreliable results" is too strong a statement since inlets can be operated (e.g., with inert materials such as Teflon and fast flow rates, etc.) to suppress inlet wall artifacts. Consider rephrasing to "sampling lines can cause unreliable results"

Line 59. "E.g. validation" please correct grammar

Line 63. Just curious - is this long-path instrument still set up, or has it been dismantled?

Line 78. replace "detection" with quantification or measurement

Line 84. The SAPHIR chamber has been described elsewhere - consider citing these papers (e.g., Fuchs et al.)

Line 95. Please define  $r$  and  $R$  (I assume they are radius of curvature and reflectivity) and use symbols different from the Pearson correlation coefficient ( $R$ , e.g., line 393). Please comment on why mirrors with a negative  $r$  were chosen since (I believe) concave mirrors are more commonly used. Also, since mirror reflectivity was measured more accurately in section 4, consider calling out this section here (rather than on line 143).

Line 134. The choice of  $\text{NO}_2$  reference cross-sections (Merienne et al. 1995) differs from what was chosen by other IBBCEAS users in this wavelength region, with Burrows et al. (1998) and Voigt et al. (2002) being popular. Considering the possibility of HONO impurities in the  $\text{NO}_2$  reference spectrum, which can lead to negative interference at low HONO/ $\text{NO}_2$  ratios as in this work (Kleffmann et al., 2006), a justification to choose the cross-sections by Merienne et al. is warranted, along with a discussion of this potential interference.

Line 143. Please add a figure showing an example calibration to the supplemental, stating the literature and observed wavelengths of the neon lamp.

Line 143. "Reflectivity calibration issues" - consider striking "issues" since (I assume) these issues were ultimately resolved.

Line 173. "gas phase titration" with  $\text{O}_3$ ?

Line 175. "by determining the corresponding NO yield from HONO numerically from the spectrum of the LEDs. The HONO photolysis contribution to NO is less than 5% compared to that of  $\text{NO}_2$ ." It is likely that the interferences are underestimated. For example, Andersen et al. (AMT 14, 3071-3085, doi: 10.5194/amt-14-3071-2021) found that "the original BLC used was constructed with a Teflon-like material and appeared to cause an overestimation of  $\text{NO}_2$  when illuminated". More recently, Gingerysty et al. (Journal of Environmental Sciences 107, 184-193, 2021, doi: 10.1016/j.jes.2020.12.011) found that in their photolytic converter the HONO to NO conversion rate "was larger than predicted from the overlap of the emission and HONO absorption spectra". Further, isoprene photochemistry in the presence of  $\text{NO}_x$  may lead to formation of PAN and MPAN (as

discussed in this paper), which are efficiently converted in the BLC due to it running hot (Reed et al ACP 16,4707, 2016, doi: 10.5194/acp-16-4707-2016). There are also potential interferences from alkenes to consider (Alam et al., AMT 13, 5977, 2020 doi: 10.5194/amt-13-5977-2020).

Line 205. Since nitric oxide was quantified, it would be informative to see those data. Please superimpose on the panels showing NO<sub>2</sub> mixing ratios.

Line 210. "At 9:15 hrs there is a marked but unexplained change in the data" which is difficult to see in the graph as presented (see comment on Figure 1 below).

Line 215. "the return to dark conditions at 15:33 hrs led initially to an unexpected increase of the HONO mixing ratio as recorded by the LOPAP instrument," which would be consistent with the LOPAP having an NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> interference, is it not? See also line 340.

Line 219. "Almost all NO was oxidised" - please show the NO data to support this statement (see line 205).

Line 224. What was the temperature of the chamber?

Line 226. "concentrations .... appeared to stagnate" - this is hard to see (see comment on Figure 1). Consider adding the time of this event to the text.

Line 243. "Vestiges" - Teflon is permeable to small molecules (O<sub>2</sub>, NO etc.) - how much NO<sub>x</sub> is leaking in from the outside?

Line 243. " The variation of temperature was limited to the natural variability. " Are the temperature data shown anywhere?

Line 246. "rather satisfactory" please be quantitative (especially since you can - see Table 1).

Line 246. "For NO<sub>2</sub> there appears to be a slight offset" and a 38% slope error - not exactly "good agreement"

Lines 289-294 - determination of  $R_{\text{eff}}$ . "to determine the reflectivity in the clean chamber instead of using  $\text{NO}_2$  as calibration gas". The description of how this was accomplished is incomplete. Please expand the text and define  $I_{\text{LL0}}$  in equation (2) and how exactly (which equation?)  $L_{\text{LL0}}$  was determined. If this procedure has been described elsewhere, cite the appropriate paper(s).

Lines 305-311 "Data evaluation" and lines 312-317 "Detection limits". These sections describe results and should precede Line 249 "Discussion". In fact, I would move Figure 4 ("Data evaluation") even ahead of Figures 1-3 as it is experimental.

Line 340. Has the potential interference from  $\text{NO}_3$  /  $\text{N}_2\text{O}_5$  in the LOPAP instrument been evaluated?

Line 347. " In the dark (closed) humidified chamber HONO can still be produced " - but the IBBCEAS did not see this ... which suggests an issue with the LOPAP ...

Line 354/355. "The inlet of the LOPAP instrument is much closer to the chamber wall" Please do not introduce new experimental details and results in a discussion section (i.e., move this information to the experimental setup section and show the LOPAP in Figure S1).

Isn't the SAPHIR chamber equipped with one (or more) mixing fan(s)? If there are gradients within the SAPHIR chamber, wouldn't have been observed and discussed in the numerous other papers using SAPHIR chamber data? If not, perhaps it should be discussed in this paper in more detail (typical mixing times etc.).

Line 400. What was the detection limit for MACR? This info is hidden in Figure S7 but should be stated here

"competitive" isn't a good choice of words since the other HONO instruments are all mobile (and this is one is not). It probably suffices to say that the LODs here are lower than those of recently described HONO instruments.

Figure 1. Please modify the figure so that the time series use the full width of the page - the scatter plots could then be superimposed as insets. In the figure as shown, the time series is crammed into a tiny corner, making it difficult to follow the discussion of the main text.

The supplemental contains a lot of figures that are not sufficiently described or discussed in the main manuscript. Please expand the text.