Anonymous Referee #1

RC1: 'Comment on amt-2021-19', Anonymous Referee #1, 22 Mar 2021

The article describes simultaneous measurements of NO_2 and HONO generated in a simulation chamber experiments by several in-situ monitors with a focus on UV LED based incoherent broadband cavity-enhanced absorption spectrometer (IBBCEAS) and its comparison against FTIR and chemiluminescent instruments. The experiments are well planned, and meticulous description of the instrumentation, measurements, intercomparisons and error analyses are provided. Well written, in a general sense, although small text corrections are sought. However, several aspects of the study need to be addressed before the paper can be accepted for publication. I suggest that the manuscript be majorly revised as per the comments listed below:

1. The diameter of the chamber is 2.13 m (page 3, line 88). Is it exactly the separation of cavity mirrors? Also, mirror radius of curvature is 2 m. Does radius less than mirror separation have any impact on cavity transmission or its stability?

Response : L=2.13 m is the exactly measured cavity mirror to mirror distance, and the mirror radius of curvature is R= 2 m, which satisfy the condition of stable optical cavity configuration: 0≤(1-L/R)(1-L/R)≤1. Therefore, the used optical cavity configuration did not have any impact on cavity transmission or its stability.

2. In section 2.3.1, it is mentioned that I_0 is measured with nitrogen or dry (zero) air in the cavity. In the equation (1) for extinction coefficient, terms for Rayleigh scattering and Mie scattering are included. I think your target samples are trace quantities of NO_2, HONO, H_2O (vapor) and CH_2O; all in gaseous state. When your I_0 already has zero air how can there be a contribution from Rayleigh scattering of air and Mie scattering by particles just by introduction of calibration gases? If your I_0 was measured in vacuum, then Rayleigh scattering by gases would be significant. I could not find any introduction of aerosol into your cavity either. Therefore, the equation (1) is misleading; also true for the equation (2) for mirror reflectivity retrieval where second term inside the parenthesis cannot be detected with dry air present in the I_0 spectrum.

Response : we agree with the reviewer, we missed some extra description for Eq.1. So, we added the following sentences at lines 201-209 on page 7 in section 2.31:

"Here $\alpha_{Ray}(\lambda)$, $\alpha_{Mie}(\lambda)$ and $\alpha_{abs-particle}(\lambda)$ are needed to consider for real atmospheric condition or open-path observation. In a particle-free environment, $\alpha_{Mie}(\lambda)$ and $\alpha_{abs-particle}(\lambda)$ can be neglected."

For Eq.2, we removed the term $\alpha_{Ray-Zero\ air}$ in equation, and added the extra narratives in line 195 in section 2.31:

"Otherwise, low-concentration NO_2 in air (<200 ppbv) was used for determination of mirror reflectivity $R(\lambda)$, the Rayleigh scattering coefficient by zero air $\alpha_{Ray-Zero\ air}$ ($\alpha_{Ray}(\lambda)$ in Eq.1) of ~10^{-8} cm^{-1} between 350 nm and 380 nm can be neglected: $\alpha_{Ray}(\lambda)$≈0, thus $R(\lambda)$ can be determined by using a known-concentration NO_2 sample as below:"

$$R(\lambda) = 1 - d\left(\alpha_{NO_2} \times \frac{I_{NO_2}(\lambda)}{I_{Zero\ air}(\lambda) - I_{NO_2}(\lambda)}\right) \qquad (2)$$

3. In fact, if one looks at figure 3 it can be seen that the Rayleigh scattering cross section is 6 – 7 orders of magnitude smaller than the absorption cross sections of the calibration and target gases. Therefore, including zero air scattering cross section spectrum in the calculations makes no sense to me. I suggest to correct section 2.3.1 appropriately.

Response : In order to provide a generally usable expression, we keep the term of Rayleigh scattering cross section in figure 3 to indicate its contribution to the total absorption in Eq. 1. In the present work, it can be neglected as indicated by the reviewer. We removed $\alpha_{Ray}(\lambda)$ in Eq. 2 in the revised version and added extra descriptions (see above).

4. On page 7, line 212, a singular value decomposition method seems to have been adopted for analyzing data. No elaboration or specifics about this method could be found in the article. It is suggested that the method is elaborated in detail or appropriate reference(s) be specified.

Response : Because this method has been widely used for concentration retrieval in IBBCEAS, two references about singular value decomposition method have been added on page 8, line 228:

Yi, H., Wu, T., Wang, G., Zhao, W., Fertein, E., Coeur, C., Gao, X., Zhang, W., and Chen, W.: Sensing atmospheric reactive species using light emitting diode by incoherent broadband cavity enhanced absorption spectroscopy, Opt. Express **24**, A781-A790, doi:10.1364/OE.24.00A781 (2016).

Varma, R. M., Venables, D. S., Ruth, A. A., Heitmann, U., Schlosser, E., and Dixneuf, S.: Long optical cavities for open-path monitoring of atmospheric trace gases and aerosol extinction," Appl. Opt. **48**, B159-B171, doi: 10.1364/AO.48.00B159 (2009).

5. How did you calculate the overall uncertainty from the individual uncertainties that you specified?

Response : the usual method to obtain the overall uncertainty u_o based on the individual uncertainties u_i is given as follows (Mathieu Rouaud, (2013), Probability, Statistics and Estimation: Propagation of Uncertainties in Experimental Measurement):

$$u_o = \sqrt{\sum_i u_i^2} \ (i=1,2,3,...).$$

6. Line 220 on page 8: It is mentioned that the statistical uncertainty from the fit was included in your error analysis. No mention was found on how this was calculated and what is the magnitude you obtained as uncertainty from the fit. How did you estimate this?

Response : The fit uncertainty was determined using statistic of 1σ deviation of all fitted residuals. 1σ deviation of the fitted residual reflected the LED intensity fluctuation and wavelength drift as well as fit error. Deduction of the uncertainty contribution from ΔI/I, the statistically related uncertainty of all 1σ deviations of the fitted residual is the uncertainty from fit. Based on the statistical uncertainty, this uncertainty is smaller than 0.5%.

The following statement was revised to address the uncertainty from the fit: "statistical uncertainty from the fit (<0.5%) (page 8, line 236)"

7. From figure 3 (b) it looks like HONO has two absorption peaks, the first one close to 355 is interfering with an absorption peak of CH_2O. In fact, after 357 nm, there is no influence (spectral interference) of CH_2O presence on NO_2 and HONO. Interestingly, the LED has an order of magnitude less power below 357 nm. If it is just the NO_2 and HONO measurements that the authors are interested in, use the spectral region from 360 nm would do the job. From figure 4 it is amply clear that in the 366 – 372 nm region, HONO and NO_2 absorption can be clearly distinguished, then what is the need to extend it to 351 nm where light intensity itself goes negligible?

Response : We agree with the reviewer's pertinent analysis. 362-372 nm region is the best spectral range for high-sensitivity measurement of NO_2 and HONO with stronger LED power and better mirror reflectivity under the present work condition that was not optimized for CH_2O measurement. The objective of this study was to investigate the possibility to make simultaneous measurements of these three species and their potential spectral interference (though the LED power was almost negligible), sensitive measurements of NO_2 and HONO were performed in the 362-372 nm region.

8. While calculating the uncertainty, were the choice of spectral (sub) intervals used for analyzing different species considered? For example, like I said in the above comment, full spectral band or a sub interval of 360 – 378 can be used to analyze for NO_2 and HONO. Would the results be the same? Could you get the same uncertainties for both spectral intervals? If different, then the error analysis must include the errors due to the choice of spectral interval. In your case, if CH_2O is the target species, then analyzing it in the 351 – 360 nm band may be desirable than the full window (of course, with NO_2 and HONO as co-analytes). If there is an effect due to spectral window choice, then optimization of the spectral interval of analysis for better results is desired.

Response : If the sub interval of 362 – 372 nm could be used to quantify NO_2 and HONO, the detectable concentrations (MDC) would be improved to be 112 ppt and 56 pptv for NO_2 and HONO, respectively. However, when using only the 351-360 nm spectral range to retrieve CH_2O concentration, MDC for CH_2O will increase from 14 ppbv (using 351-378 nm spectral) to 41 ppbv. Based on the fitted residual at the different wavelength ranges, the different 1σ residual values depending on wavelength range have been added into the Fig. 4(c) for MDC estimation, the corresponding text in section 2.3.1 page 8, lines 242-244 has been also revised. The corresponding statement on the MDC has been revised as follows:

"Based on the fitted residual, the corresponding 1σ minimum detectable concentration (MDC) for 120 s integration time are 112 pptv for NO_2 and 56 pptv for HONO using the 362-372 nm region data. MDC for CH_2O with 120 s is 41 ppbv using the spectrum in the 351-360 nm region."

While the MDC is only 41 ppbv if the narrower spectral region of 351-360 nm was used to CH_2O concentration retrieval due to weaker LED emission intensity in this range (blue curve in Fig. 2(a)).

9. In the section 2.3.2 on page 8, FTIR spectral analysis is described. Spectral fit in support of FTIR measurements, like corresponding to figures 3 and 4 for IBBCEAS instrument, needs to be shown.

Response : The FTIR data obtained here results from the analysis of 679 individual spectra. In order to minimize the effect on interfering species and following a similar approach to what is done in remote sensing, each of these spectra has been divided in small spectral windows in for which the fit was perform separately. We could show one or some of these windows for one of a few of these spectra, but this would not inform the reader about the robustness of the whole data analysis. Further, the HONO are sometime 20 times (or more) smaller than the water line. This would be a problem if the fit would involve wide

absorption band – like it is the case in the UV domain – but here the spectra are highly structured which allow the fit procedure to have enough sensitivity to distinguish well between the various species. We have tried to produce the requested graph but, despite obvious mathematical sensitivity, the results are not spectacular enough to be evaluated with naked eyes.

Furthermore, the FTIR analytical procedure is not the central topic of the present paper as this technique is employed in simulation chamber since the mid-80's and routinely used in the LISA research group since 1997 (see, eg. Doussin et al, 1997). We believe that giving too many details about this part of the work would dilute the main message of the paper that is about the use of an in-situ CEAS system in a simulation chamber.

Some graphs have been produced (see below) but we don't think it is relevant to add them to the paper as we believe that it is more appropriate to keep the focus on the IBBCEAS development.
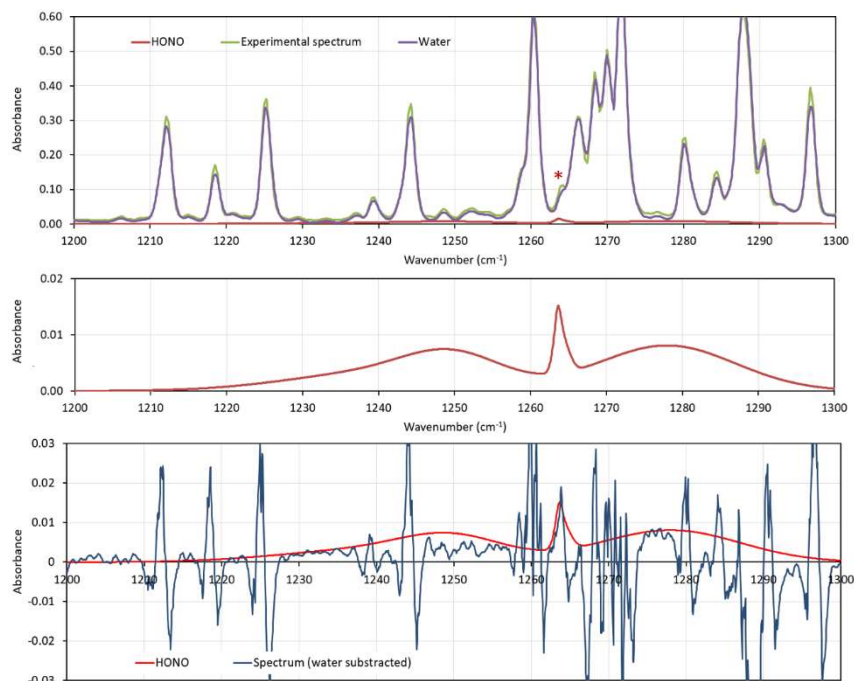

Figure 1 Spectral fit of the HONO bands in the 1200-1300 cm^{-1} region. The red * in the first panel indicate a key feature of the HONO spectrum: the nu-3 band of the trans HONO-isomer at 1263 cm^{-1}. Second and third panel is the Barney et al, 2001 spectrum scaled to 52 ppbv under our experimental condition and compared in the third panel to the experimental spectrum after water subtraction.

10. In this study authors used "synthetic" reference spectrum by Barney et al., 2001, for analyzing HONO from FTIR measurements. On page 10, line 303, the authors mention that the use of a different cross section for HONO introduced a larger error. Could you do an error analysis for FTIR measurements similar to that performed for IBBCEAS as well and add to the paper?

Response : What is meant here is that HONO is a complex molecule to handle in the lab because of heterogeneous formation as well as because of destruction processes. In consequence, the values of its absorption cross sections are still a matter for discussion as recalled by Gratien et al, 22009 (cited). Obviously, the use of imprecise cross sections leads to systematic errors. Our analysis of the state of the

knowledge on this topic is that the work of Barney et al, 2001 is among the more reliable evaluation of the infrared cross section of nitrous acid.

In addition, the use of synthetic spectrum as the advantage - in comparison with the use of homemade reference spectrum – to avoid bringing more instrumental noise in the spectral fit which would increase the random errors.

Further, the risk of having traces of NO_2 in an experimental reference spectrum is not negligible which can bring cross-estimation errors.

The FTIR in-situ use in chamber is quite well-known since a long time; It is known that we are working here at the limits of its capabilities and why it is interesting to develop new techniques such as IBBCEAS.

Having said this, again, we believe that the paper is more oriented toward the description of the IBB-CEAS system than the in situ FTIR and that a thorough error analysis for FTIR measurements is beyond the scope of this paper.

11. On page 9, line 274, comparison between IBBCEAS and FTIR measurements is specified. Although the discrepancy between the measurements is attributed to lower detection sensitivity of FTIR, the measurements of concentrations at well above detection limits show considerable deviations (Figure 7c). So, this is not the reason as mentioned in the paper. Either the FTIR is underestimating the NO_2 concentrations due to some bias or the IBBCEAS is overestimating. Spectral fit from FTIR would help in this situation to assess the spectral validation of the measurements. I would tend to believe IBBCEAS measurements, more so because its calibrations and spectral validations are provided whereas less information regarding FTIR spectra and fit are provided in the paper. Error bars are given for IBBCEAS side, but no uncertainty analysis seems to be available for FTIR. This needs to be addressed better than attributing deviations to lower sensitivity of FTIR. Lines 339-340 in the section 4 (Conclusions) need to be corrected accordingly.

Response : Because of the presence of many strong water lines under the condition of the experiment in the 1500-1900 cm^{-1} region, the spectral region used to estimate NO_2 concentration was 2830-2950 cm^{-1} which is far from exhibiting similar intense NO_2 absorption. In consequence, the typical detection limit of 5 ppbv in this system were not relevant anymore (this has been corrected in the text). The standard deviation due to the random errors is certainly rather in the range of 10 ppbv lead to and uncertainty of ca. 20 ppbv as can be confirmed from the plots of Fig. 7. When considering a random error of ca. 20 ppbv, the differences between IBBCEAS measurements and FTIR measurements become truly difficult to discuss.

This was not unexpected and this is why we relied on the chemiluminescence analyzer NO_2 data (if corrected from HONO interferences) which fit well with IBBCEAS measurements.

12. This paper has both FTIR and IBBCEAS mounted on the wall of an atmospheric simulation chamber with two separate pieces (like a transmitter-receiver arrangement or the like) with atmosphere in-between. This is done to directly use atmosphere as sampling volume and avoid sampling losses in extracting it into a containing volume. This is a step towards applying this technique into the real atmosphere. However, the real atmospheric conditions may have other interfering gases and suspended aerosol (absorbing, non-absorbing, SOA, etc.). Many atmospheric simulation chamber experiments assessing such measurement methodologies specify the instrument performances under varying

atmospheric conditions. How would your measurement sensitivity be affected in the presence of aerosols in the chamber?

Response : Yes, you are right. In the case of aerosols present in the chamber, when the Mie scattering and absorption by particles, $\alpha_{Mie}(\lambda)$ and $\alpha_{abs\text{-}particle}(\lambda)$, become similar to, or even higher than the mirror loss $(1-R(\lambda)/d))$, they are no longer negligible which might strongly shorten the wavelength-dependent effective cavity path length, and thus decrease the measurement sensitivity of the target species.

13. Finally, a few suggestions for text edits:

a. On page 2, line 43, "topics" to be replaced by "topic"
b. Line 52, "following" to be replaced by "followed"
c. On page 6, line 163. The sentence starting with "When NO2 concentration …." is incomplete.
d. Line 168. The sentence starting with "As described …" is incomplete.

Response : All these typo or grammar errors have been corrected. Thanks!