Anonymous Referee #2

RC2: 'Comment on amt-2021-19', Anonymous Referee #2, 12 Apr 2021

The paper describes a IBBCEAS which, on the contrary to many existing set-ups, introduces the innovation of its in-situ installation, avoiding unwanted invasive use of pumps, etc. The system can measure HONO and, simultaneously, NO_2 and CH_2O. To evaluate its performance, an intercomparison against other instruments, NitroMAC, FTIR and NOx monitor is carried out. The paper is well written and results are well discussed. There is a detailed description of the instrumentation, procedures and error analysis. For these reasons I recommend its publication after considering the following aspects:

24: The title says HONO, NO_2 and CH_2O, but the introduction mainly talks about HONO. HONO measurement is challenging, while the detection of NO_2 and CH_2O is better stablished. Nevertheless, I would suggest to either include brief information on NO_2 and CH_2O or explain that the main interest is measuring HONO although NO_2 and CH_2O absorb in the same region and are also tracked, being an advantage of the technique.

Response : We agree with the reviewer's opinion, the following sentences have been added in the introduction section (page 3, lines 69-72):

"Although the main interest for current work is to measure HONO, NO_2 and CH_2O are two other important atmospheric species (Washenfelder et al., 2016; Liu et al., 2020), these two molecules have strong absorption in the same region. Simultaneous measurements and quantification of HONO, NO_2 and CH_2O can be performed by the IBBCEAS techniques (Wu et al., 2014; Washenfelder et al., 2016; Duan et al., 2018; Jordan et al., 2020)."

80: This work introduces some changes in the set-up of the instrument, but it is based in previously developed IBBCEAS. Please, add some references.

Response : Four references related to previously reported IBBCEAS (Gherman et al., 2008; Fuchs et al., 2010; Wu et al., 2012; Wu et al., 2014; Duan et al., 2018; Jordan et al., 2020) have been added into section 2.3.1 of the revised manuscript (page 7, line 198-199):

There are only two references related to measurements of NO_2 and HONO in simulation chamber (Gherman et al., 2008; Fuchs et al., 2010). Two recently published papers reporting on measurements of NO2 and HONO in ambient air have been added as references:

Duan, J., Qin, M., Ouyang, B., Fang, W., Li, X., Lu, K., Tang, K., Liang, S., Meng, F., Hu, Z., Xie, P., Liu, W., and Häsler, R.: Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and NO_2, Atmos. Meas. Tech., 11, 4531–4543, doi:10.5194/amt-11-4531-2018, 2018.
Jordan, N. and Osthoff, H. D.: Quantification of nitrous acid (HONO) and nitrogen dioxide (NO_2) in ambient air by broadband cavity-enhanced absorption spectroscopy (IBBCEAS) between 361 and 388 nm, Atmos. Meas. Tech., 13, 273–285, doi:10.5194/amt-13-273-2020, 2020.

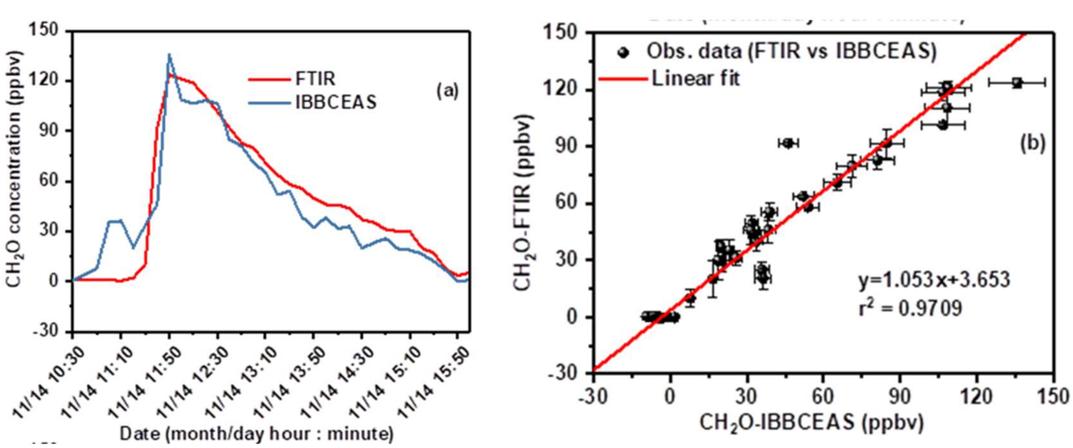
225: Can you confirm that DL for CH_2O is 5 ppb? The emission of the LED below 356 nm is very low (Fig 3). The absorption for 143 ppb in Fig 4 doesn't seem to suggest that an absorption of 5 ppb will be detectable with such noise. DL has been calculated from 1-σ in Fig 4 through the region 351-378 nm as it is the analysis region, but 1-σ in the region where CH_2O absorbs is much higher, therefore, the real DL would be higher. That noise would also explain the noisy profile in Fig 9. Please, comment.

Response : Spectral region of 351-378 nm was used to fit, when we calculated 1σ minimum detectable concentration (MDC) for HONO and NO_2, we used 362-372 nm residual data. But for CH_2O, the spectral data of 351-360 nm was used to estimated 1σ MDC. MDC (or DL) for CH_2O should be 41 ppbv not 5 ppbv with 120 s. We have corrected this error. The corresponding text in section 2.3.1 page 8, lines 242-244 has been thus revised as follows:

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

580: There are -15 ppb of CH_2O in Fig. 9. It might be due to interference with HONO. On the one hand, in general, these unrealistic data can be withdrawn as they are below the DL. Indeed, those data seem to have been withdrawn from Fig. 9b since, looking at the 0 ppb of concentration for IBBCEAS, data for NITROMAC do not replicate the whole set of data in Fig. 9a, so they can be removed from Fig. 9a. On the other hand, they give information on how HONO is interfering, therefore, if the authors decide to include these data, some comment should be made in the text.

Response : Based on our updated analysis, 1σ minimum detectable concentration (MDC) for CH_2O is about 41 ppbv with 120 s, the data of about -15 ppbv of "CH_2O" in Fig. 9 before the introduction of CH_2O sample (without CH_2O) are below the MDC, thus these unrealistic data before injection of CH_2O have been withdrawn in the revised Figure 9a, as shown below. Because the measured CH_2O concentration below 41 ppbv is not accurate. In the revised version, some unrealistic data have been withdrawn.



157: There were 4 experiments. At the beginning, the first experiment is described, and in line 174, it is said that there were 4 days of experiments. It can be mentioned that they were done under the same conditions as the first one.

Response : Yes, the 2^{th} to 4^{th} experiments were performed under the same experimental conditions as the first one. The procedures for 4 experiments were the same: firstly, the simulation chamber was pumped and evacuated to a pressure of ~ 1 mbar; secondly, the simulation chamber was filled with zero air to 1 atm (1000 mbar); and then, NO_2 (<150 ppbv) sample was injected into the chamber for mirror reflectivity determination; finally, H_2O vapor (<1.86%) were introduced into the chamber for HONO generation. During the whole experiment, IBBCEAS, NITROMAC, FTIR, NOx analyzer, temperature and relative humidity sensor (T&RH sensor), pressure sensor were running to record all related data for later analysis. The following description was added on page 6, lines 176-177 to describe the experiment procedure:

"There were 4 experiments during the whole measurement, the 2th to 4th experiments were performed under the same experimental conditions as the first one. The four experiments were followed by the same procedure."

172 and 198: Cavity mirror reflectivity is a key parameter in IBBCEAS for calculating the concentrations of the target molecules. Having a NO_2 monitor, why did you use FTIR for its determination? The NOx analyzer shouldn't have interferences during calibration as NO_2 pure is introduced and there is no NOy (unless RH was not zero in the chamber). Is it related to accuracy? Please, add some comment.

Response : Because the RH in the chamber was not ideally zero, residual H2O vapor always existed inside the chamber, the estimated residual H_2O concentration is about 0.002% to 0.01% from T&RH sensor and FTIR. Once NO_2 was introduced into the chamber, unknown-concentration NOy would be generated immediately. As discussed in the later section, positive interferences can't be avoided. So FTIR spectrometer was used to determine NO_2 concentration for get more accurate mirror reflectivity in the present work.

240: Table 1 reflects the spectral regions corresponding to the IBI. Are these the analysis regions used for the analysis of each compound? If not exactly, please include this information in Table 1 or in the text.

Response : The table has been revised accordingly and the spectral windows used for the FTIR data analysis have been added.

255: Rephrase: "and 120 such acquisition data"… to "and 120 of such acquisition data" or "120 data acquired in this manner were"

Response : thanks reviewer for such helpful revision, correction has been done with "120 data acquired in this manner were".

276: detection limit of 10 ppbv at a sampling time of 1 min, compared …. (or similar, to distinguish from DL of 5 ppb at sampling time of 5 min in line 130).

Response : Agree with the reviewer, we corrected this typo error. The sentence is changed to "MDC of 10 ppbv at a sampling time of 5 min compared to that of 112 pptv in 2-min for IBBCEAS" (page 10, lines 301-302).

277: In Fig 7a, NO_2 by FTIR is underestimated when there is CH_2O. Was CH_2O included as pure reference spectra in the analysis of NO_2?

Response : First of all, we thank the reviewer for having spotted this. Indeed, 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}. The choice of this region had two consequences:

- as the 2900 cm^{-1} region is far from exhibiting similar intense NO_2 absorption, the random error from the NO_2 quantitation was brought to ca. 20 ppbv.
- while CH_2O was systematically included as pure reference spectra in the analysis leading to NO_2, there seem to be an interference between the two species during the fit. We double check this but it seems that this effect is rather due to some noise addition from the subtraction of the HCHO reference spectrum which is an experimental spectrum (and not a calculated one) and so which contain some noise.

This was not totally 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.

295: The reference from Stutz is widely used by the scientific community showing good agreement with others, but not with Brust. Apart of the error due to using different HONO references, the hypothesis of the mixing fans makes sense, and then I wonder: it would imply that also in the first peak in Fig 7 the mixing fan speed was increased since NitroMAC tracks FTIR data as in the 4th peak, while it doesn't in the 2-3rd peaks. How was the mixing fan in the day of the first peak?

Response : Unfortunately, at the time of these experiments there was no recording of the mixing fan speed and the current brought to the mixing system electric motor was manually adjusted. The lab notebook only reports a change in the setting in the morning of the 4th peak days.

This set of experiments has latter led the CESAM group to implement the recording of the fan mixing speed that is operational now (but too late to support the hypothesis made here).

300: "NitroMAC values were slightly larger than IBBCEAS". Slope NitroMAC vs IBBCEAS is 1.27, I would remove the word slightly.

Response : Agree with the reviewer, we have deleted the word "slightly"

325: "relative low detection limit" do you mean high instead of low?

Response : Agree with the reviewer, we have corrected "low" to "high".

334: The authors might comment on how feasible is to use this in-situ system in other chambers.

Response : The current approach can be easily extended to application in other chambers for in-situ optically "watching" chemical reaction without introduction of any disturbance. The challenge is how to keep high precision, enough temporal resolution, and good stability if the harsh experiment condition happens, such as aerosols or other suspended particles are introduced into the chamber.

575: Fig 8c, HONO IBBCEAS doesn't have error bars.

Response : HONO from IBBCEAS has error bars, but the magnitude of its error bar is much smaller than that of HONO from FTIR, because the measurement precision of IBBCEAS is about 100 times better than that of FTIR. BTW, three wrong error bars for HONO from IBBCEAS in Fig. 8b have been corrected as well.

575: Did the authors try to analyze HONO (and NO_2) in the region 357-380 nm? To analyze CH_2O, the selected region is adequate as both the HONO absorption at 368 nm and NO_2 in the whole region help in a better calculation of the HONO fit, and therefore, the error due to the interference of HONO around 353 nm when calculating HCHO is reduced. But, to analyze HONO and even NO_2, the absorption of HONO at 368 nm is high enough to determine it in 357-380 nm, and it would avoid the interference with CH_2O in a region with high noise. Would Fig. 8(a) be the same?

Response: Based on the fitted residual (Fig. 4(c)), using the 362 – 372 nm spectral to analyze NO_2 and HONO, MDC for NO_2 and HONO will be improved to 112 pptv and 56 pptv, respectively. For CH_2O measurement, 351-360 nm spectral range is used to retrieve CH_2O concentration, the MDC for CH_2O will be 41 ppbv with 120 s. Based on the analysis, the corresponding text in section 2.3.1 (page 8, lines 242-244) have been revised as follows:

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

Some editing comments:

80 and 87: installed on à installed in
108: reagent as soon as a few à reagent a few?
115: standard solutions was à standard solutions were
126: (see Fig. 1-insert) à (see Fig. 1)
155: 370), a FTIR spectrometer à 370) and a FTIR spectrometer
157: The experiment, the experiments or the first experiment?
163: Check sentence "When…"
168: Check sentence "As described…"
175: allows à allow
268: between two instruments à between the two instruments
279: weighed à weighted
565: Figure 6, X axis. Month (not moth)

Response : All these editing errors have been corrected.