Anonymous Referee #3

RC3: 'Comment on amt-2021-19', Anonymous Referee #3, 22 Apr 2021

Reviewer 3 (particular thanks to the reviewer for the careful reading and revision)

This manuscript reports an open path setup established at the CESAM simulation chamber in Paris, which is based on Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS). This instrument for the detection of HONO, NO_2 and CH_2O is compared with other experimental approaches "NitroMac" and more conventional chemiluminescence detection as well as FT-IR spectroscopy. The performance of the instruments is characterized, and aspects of the instruments' advantages and drawbacks is discussed on basis of measurements taken in the course of a 3-day campaign.
The content of the manuscript is quite appropriate for the special issue on Atmospheric Simulation Chamber Research, instrument intercomparisons should be of general interest to the respective community. The manuscript is however not particularly well written as far as the use of the English language is concerned. In many sentences it was not very clear what the authors were trying to say. This should be improved in the final version of the submission (see the attached file, where also more comments can be found for the benefit of the authors).

Response : Thanks very much for the reviewer's valuable suggestions, we have carefully checked the English usage.

Other shortcomings are: There is a lack of detail in some parts. E.g. the retrieval of data (from the NitroMac machine and FTIR spectrometer) could have been discussed somewhat better. The discussion of systematic errors and of errors in general are of interest to the community and could have been done in more detail and more quantitatively. The role of aerosol was not even mentioned in the discussion – it is important in the context of the data retrieval and limits of detection. There is certainly not enough reference made to the relevant literature. The citations appear to be incomplete. The manuscript exclusively describes technical aspects of the detection setups for HONO, NO_2 and CH_2O and does not report or discuss any new atmospheric or gas phase processes in the context of HONO formation or destruction, in other words, the advancement of science is minimal, but this was obviously not the main objective of this work.

Response : We revised the whole manuscript according to the reviewer's comments one by one as follows.

1. Page 1, line 16, "1-σ" reads strange, should be 1\sigma.

Response : corrected to "1σ".

2. Page 2, line 32, "one mostly possible heterogeneous" English usage.

Response : corrected to "the most possible heterogeneous".

3. Page 2, line 51, "... are sensitive. What does "sensitive" in this context mean. This is merely qualitative."

Response : Please see the answer in next response.

4. Page 2, lines 51-53, “They generally rely on conversion of HONO into nitrite ion (NO^{2-}) following by absorbing dye conversion (Kleffmann et al., 2006) and may be susceptible to chemical interferences and sampling artifacts (Stutz et al., 2010).” English usage.

Response : the statement has been revised as follows (Page 2, lines 51-55): "In wet chemical methods, HONO is sampled on aqueous/humid surfaces and converted into a species suitable to be analyzed with conventional chemical analytical techniques such as ion chromatography (IC), fluorescence (FL), chemiluminescence (CL), long-path absorption photometer (LOPAP) or high-performance liquid chromatography (HPLC)" (Chen et al. 2013). These wet-chemical-based instruments often suffer from unquantified chemical interferences and sampling artifacts (Stutz et al., 2010)."

W. Chen, R. Maamary, X. Cui, T. Wu, E. Fertein, D. Dewaele, F. Cazier, Q. Zha, Z. Xu, T. Wang, Y. Wang, W. Zhang, X. Gao, W. Liu, F. Dong, “Photonic Sensing of Environmental Gaseous Nitrous Acid (HONO): Opportunities and Challenges,” in *The Wonder of Nanotechnology: Quantum Optoelectronic Devices and Applications*, M. Razeghi. L. Esaki, and K. von Klitzing, **Eds**., SPIE Press (ISBN 9780819495969), Bellingham, WA, pp. 693-737 (2013)

5. Page 2, lines 62-64, “frequently, intercomparison between in point and long-path measurements exhibited significant discrepancies with uncertainties of 10%-25% for HONO concentrations from ten-pptv to ten-ppbv range.” This is too unspecific.

Response : Some description is not accurate and lack of results citation, the sentence has been corrected to (Page 3, lines 65-66) “frequently, intercomparison between in point and long-path measurements exhibited significant discrepancies with uncertainties of about 20% (Pinto et al., 2014; Kleffmann et al., 2006) in HONO concentrations varying from ten-pptv to ten-ppbv range”.

6. Page 3, lines 69-70, “instrument for simultaneous measurement of wider concentrations at natural conditions of HONO (100 pptv-30 ppbv), NO_2 (100 pptv-120 ppbv) and CH_2O (3-150 ppbv)”. What motivates the ranges stated here. Seems in contradiction with the abstract.

Response : it is now stated as follows in order to avoid any confusion (like "generation of their concentrations in a wide range"): "evolution of concentrations of HONO (0-30 ppbv), NO_2 (0-120 ppbv) and CH_2O (0-150 ppbv) in a wide range has been optically tracked using a single IBBCEAS device in the present work.

Abstract, page 1, lines 16-18: “1σ (SNR=1) detection limits of 112 pptv for NO_2, 56 pptv for HONO and 41 ppbv for CH_2O in 120 s were found for the UV-LED-IBBCEAS measurement approach”.

Page 3, lines 74-75 : “instrument for simultaneous measurement of HONO (0 pptv-30 ppbv), NO_2 (0 pptv-120 ppbv) and CH_2O (0-150 ppbv).”

7. Page 3, line 83, “plate”. What is the divergence of the LED. What optical power was used for the experiment? What is the shape and spectral with of the LED's spectrum? This is not mentioned here but it is in Figure 3 it seems. The spectrum looks like it is affected by a filter - it that correct?

Response : “plate” was corrected to “block”.

LED emission area was about 1 mm^2 with a divergence angle of about ±60°, according to the datasheet. LED emission power was about 300 mW. The distance between LED and L2 (with diameter *d*=25.4 mm) was about 100 mm, which leads to an estimation of the used power of about 66 mW in the experiment. The shape of the LED emission spectrum was as shown in Fig. 3(a), experimentally recorded in the present work. The measured LED spectrum shapes were the same with and without filter, not affected by filter.

8. Page 3, lines 88-89, "on the simulation chamber walls". I guess they were on mirror holders and not on the walls.

Response : the cavity mirrors were indeed installed directly on the flanges attached to the simulation chamber walls, as shown in Fig. 2. On the mirror holders are installed the used focusing lens (L2) and the optical filter.

9. Page 3, line 92, These are effective pathlengths.

Response : yes, they are effective pathlengths. "equivalent" is replaced by "effective".

10. Page 3, line 93, L1 not shown in Figure 1. It is called L2. Over 30 nm one may want to consider a doublet (achromatic lens). How far from the LED was the lens placed? This distance is crucial. If the light was focussed (as stated), then what was the magnification of the first image in the cavity? Note, the authors have not mentioned the divergence of the LED and hence it is not clear how much optical power could actually be used for the IBBCEAS experiment. Where was the focal point.

Response : Yes, you are right (thanks for the careful review): L1 should be L2 (corrected). In reality, L2 and L3 were all indeed achromatic lens (now mentioned clearly in the revised manuscript). The distance between L2 (*f*=75 mm) and LED was adjustable (in the range of 80-100 mm) such that the focal point was located near the center of the optical cavity. The magnification of the first image in the cavity is about 10 times.

Answers to the questions about LED are provided above in Question 7.

11. Page 3, line 94, What is the suppression of the filter at 390 nm (and at 340 nm)? From Figure 3 it is not clear that these band-pass filter specs are appropriate since the reflectivity spectrum is only shown up to 380 nm.

Response : A 340-390 nm filter lets pass the used LED emission (350-380 nm, Fig. 3(a)) and cuts off the undesirable wavelengths ($\lambda < 340$nm or $\lambda > 390$ nm) out of the high-reflectivity range of the cavity mirrors in order to avoid CCD saturation due to the lower mirror reflectivity in these wavelength regions.

12. Page 4, line 96, "L2 (BK7, f=75 mm)". Contradicts the labelling in Figure 1.

Response : right, it should be L3, corrected.

13. Page 4, line 97, Was the spectrometer temperature controlled? Was it cooled at all? Temperature stabilization is important to avoid wavelength drifts.

Response : The temperature of the used CCD spectrometer was controlled by a thermoelectric cooler (TEC) and cooled down to 40 °C (30-43 °C) below the ambient temperature to avoid wavelength drifts as well as to remove dark noise and readout noise. The following statement is added in the revised MS (page 4, lines 103-105): "Temperature of the used CCD-camera was controlled at 40 °C below ambient temperature to avoid emission spectrum drifts as well as to remove dark noise and readout noise."

14. Page 4, line 98, Was the spectral resolution measured? Where does it come from?

Response : The spectral resolution was determined by experimental measurement of emission line from a known light source, AS-363 Xenon lamp. The value of 0.59 nm was obtained for a width of 50 µm of the used CCD entrance slit.

15. Page 4, line 102, "semi-continuous", What is meant by semi continuous? This is rather unspecific.

Response : Here "semi-continuous" means that the instrument was developed to measure HONO during intensive field campaign or field deployment lasting from 1 to several months. Being based on an online chromatographic technique, it alternates a sequences of sampling periods and analytical period, but this has been described in detail in Afif et al, 2016 (cited) and is not the topic of the present paper. For clarity, we removed this term ("semi-continuous") from the revised manuscript.

16. Page 4, lines 114-115, "from integration of the peak and a calibration calculation." rather unspecific

Response : We modified this statement as follow in the revised manuscript (page 4, lines 121-124):

"The response obtained by integration of the chromatographic peak for the second stripping coil l is then subtracted from that of the first one to eliminate interferences. HONO concentrations are then calculated from this net signal using calibration factors determined through direct calibrations of the analytical system (HPLC-UV-Visible) performed using NaNO2 standard solutions."

17. Page 4, line 124, "effective", In a White cell this is not an "effective" but a "true" pathlength.

Response : Following reviewer suggestion, we deleted the term "effective" for White cell.

18. Page 4, line 126, "(see Fig. 1–insert)", The angle is not evident from Figure 1. Figure 1 needs to be improved in that regard.

Response : The figure 1 has been updated and an insert has been added to show a schematic view from the top showing the angle between the two in-situ spectrometric pathways.

19. Page 5, line 130, What are these detection limits based on? Absorption at specific individual wavelengths of the target species, or is it based on fits of bands in the recorded spectra?

Response : The detection limit is given as indicated value only. They are based experimentally on the fit and they take into account not only the specific absorption of the considered molecules but also the noise level on the condition of the experiments (quality of the alignment of the system, chosen integration time …. as well as the presence of interfering species (e.g. water, CO_2 …. etc). Thanks to reviewer's remarks we have spotted that the detection limits was not related to the spectra window used in this study. We have hence modified the text accordingly.

20. Page 5, line 135, “catalyzed converter”, The converter itself in not catalyzed. What are you trying to say?

Response : Agree with the reviewer, the statement is modified as: "via a heated molybdenum-converter,"

21. Page 5, line 148, What are the errors here?

Response : “The measurement error was 1% for RH and 0.1 °C for temperature at atmospheric pressure and room temperature.” (page 5, lines 156-157) was added.

22. Page 5, lines 152-153, “it provides a 2 m long diameter”, I am not getting this, I am afraid.

Response : the statement is revised as: “it provides a 2 m length as physical base length for both the FTIR's White cell and IBBCEAS' cavity"

23. Page 5, line 156, A schematic drawing of the position of the instruments would be helpful here.

Response : We updated figure 1 to give a better schematic drawing of the position of the instruments.

24. Page 6, lines 163-164, “When NO_2 concentration inside the chamber stabilized at 120±5 ppbv, water vapor produced in a small pressurize stainless steel vessel filled with ultrapure water (18.2 Mohm, ELGA Maxima).”, this sentence does not make sense - check the English. "was filled" ???

Response : This sentence is revised (page 6, lines 172-174): “A pressurize stainless steel vessel filled with ultrapure water (18.2 Mohm, ELGA Maxima) was used to produce water vapor. When the NO_2 concentration inside the chamber was stabilized at 120±5 ppbv, H_2O vapor was introduced into the simulation chamber.”

25. Page 6, line 167, “a significant gas-phase HONO is systematically observed.”, Improve the English

Response : “a significant gas-phase HONO is systematically observed.” is changed to “a significant amount of gas-phase HONO is systematically produced for the present investigation work”

26. Page 6, line 168, “As described in the literature (Finlayson-Pitts et al., 2000; Lammel et al., 1995; Spataro et al., 2014).”, This sentence is misplaced here it seems. Also improve the English.

Response : The statement is modified as: “As stated in the literatures (Finlayson-Pitts et al., 2000; Lammel et al., 1995; Spataro et al., 2014), HONO is generated through ….”.

27. Page 6, lines 175-176, “was performed to allows the investigation of the sensitivity of the UVIBBCEAS data analysis to the interferences in the UV range.”, English.

Response : “allows” was corrected to “allow”: "was performed to allow the investigation on the sensitivity of the UV-IBBCEAS data analysis to the spectral interferences in the UV range".

28. Page 6, lines 180-181, “This process explains the peak shape formed of a straight injection step followed by an exponential decay of the various experiences.”, This sentence is misplaced here it seems. Also improve the English.

Response : It's modified as: “This process explains the observed peak shape resulting from a straight injection step followed by an exponential decay during four-day experiments (1st to 4th peaks in Fig.7 (a) and Fig. 8 (a)).” And this sentence was moved to “Results and discussion” section on page 9, lines 273-275.

29. Page 6, line 188, certainly also older, more original IBBCEAS literature should be cited here.

Response : References “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 the revised manuscript on page 7, lines 198-199.

30. Page 7, line 190, The mirrors were not purged - why?

Response : Because our measurements were performed in a clean and particle-free chamber, the cavity mirror reflectivity *R* (λ) was not significantly changed (within an uncertainty < 0.5%) which was checked before and after each experiment (2nd to 4th peaks in Fig. 7(a) and Fig. 8(a)). If particles are present in the chamber, purging cavity mirror would be necessary to prevent contaminants on the mirrors.

31. Page 7, 197, “To do so”, English

Response : “To do so” has changed to “In order for determination of *R* (λ)”

32. Page 7, line 200, “the real cavity length *d*”, Why would you retrieve the cavity length from a fit? That gives you one more fit parameter which might even correlate with some of the other "true" fit parameters. This is not meaningful in my opinion.

Response : “the real cavity length *d*” is not determined from a fit. This sentence is changed to “the mirror-to-mirror distance of the optical cavity *d*”.

33. Page 7, line 211, “(number densities n_{NO2}, n_{HONO}, n_{CH2O}, a, b and c)”, d is not mentioned here as fit parameter?

Response : “*d*” is the distance between two cavity mirrors (d=2.13 m) and is not a parameter to fit.

34. Page 7, line 212, What was the best fit range? 350-380 nm? Did you take the entire spectrum?

Response : We recorded the entire spectrum of 290-480 nm. But only the LED emission region of 351-378 nm were used for fit.

35. Page 7, lines 214-215, "during data recording with the software procedure which is comparable to the discussion on the IBBCEAS set-up evaluation", What are you trying to say here?

Response : The statement is modified as (Page 8, lines 230-232) : Acquisition time for each spectrum was 2 minutes, the statistical error of each individual spectrum is close to ~1%. This ~1% statistical error is as good as the results reported in the references for other IBBCEAS setups (Kleffmann et al., 2007; Fuchs et al., 2010; Varma et al. 2009; Gherman et al., 2008; Rodenas et al., 2013; Min et al., 2016).

36. Page 7, line 216, Varma et al. 2009 clearly missing here. Other original IBBCEAS literature and LOPAP literature in the context of chamber work is also not cited in this publication and should be included. e.g. Kleffmann and co-workers, Ruth and co-workers, Brown and co-workers ... Some related studies at CEAM (Valencia) and SAPHIR (Juelich) also seem to be missing.

Response : References including Kleffmann et al., 2007; Fuchs et al., 2010 (Brown and co-workers, SAPHIR, Juelich), Varma et al. 2009 (Ruth and co-workers); Gherman et al., 2008 (Ruth and co-workers) and Rodenas et al., 2013 (CEAM, Valencia) have been added at the right places in the updated manuscript.

37. Page 8, line 222, "351 to 378 nm", was that the fit range?

Response : Yes, 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."

38. Page 8, line 225, The stated values are all mixing ratios by volume.

Response : We use the uniform way of "ppbv (part per billion by volume)" and "pptv (part per trillion by volume)" in the revised manuscript.

39. Page 8, line 229, "1 s per spectrum", The other way around: 1 spectrum per second

Response : correcting "1 s per spectrum" to "1 spectrum per second".

40. Page 8, line 233, Why is there no minimum observed in the Alan variance plot? Do the authors have an explanation for this? What make them select 120 s as integration time? Where is the "compromise"?

Response: In our investigated time range of 180 s, these linear Allan variance plot shows a White noise dominant regime for the developed IBBCEAS system. Using longer integration time (for example, 1000 s), the minimum will be observed in the Alan variance plot. Here, as a compromise between detection limit (requiring long integration time) and measurement time response (requiring short measurement time), an integration time of 120 s was selected for use in the present work.

41. Page 8, line 235, What kind of apodization (if any) was used?

Response : The apodization function used is “Happ-Genzel”. This has been added in the text

42. Page 9, line 255, “datum”, ? data point?

Response : “datum” is changed to "spectrum"

43. Page 9, line 256, “response time”, What is the "response time"? The integration time?

Response: “response time” corrected to " integration time "

44. Page 9, line 259, “committed”, ?? what do you mean here. "executed"?

Response: “committed” changed to "performed".

45. Page 9, line 263, “positive”, What is meant by a "positive interference". What is meant by "positive"?

Response: “positive” means NO_2 concentration measured by NOx analyzer is higher than the real NO_2 concentration, i.e. NOx analyzer overestimates NO_2 concentration.

46. Page 9, line 266, “After correction of the HONO contribution”, How was this done. Was HONO measured at the same time? More detail is necessary here on the correction procedure. Is there an explanation as to why the times associated with the loss of NO_2 are time dependent for the NOx analyzer? What are the losses due to? Wall losses, or was the chamber continuously purged?

Response: The following sentences below are added in the revised MS to explain how this correction was done (page 10, lines 288-291): “The amount of the overestimated NO_2 concentration was attributed to HONO contribution that was simultaneously measured by NitroMAC. The real NO_2 concentration was then obtained by deduction of the HONO concentration measured by NitroMAC from the NO_2 concentration measured by NOx analyser.”

The loss was mainly due to wall losses.

47. Page 9, lines 268-269, “Total intercomparison measurements”, What is a "total intercomparison measurement". Total?

Response: “Total intercomparison measurements of NO_2 have been then compared” has changed to “Measurements of NO_2 have been then compared”

48. Page 9, lines 272 and 274, “98.65% and 88.47%”, Should not be stated in %

Response: Using “0.987 and 0.885” to replace “98.65% and 88.47%” for correlation coefficient of r^2. All other similar data were also corrected to the decimal digits without %.

49. Page 9, line 273, “,”, Full stop. Two sentences.

Response: Corrected

50. Page 10, lines 293-294, “this difference is close from the measurement errors.”, close from? What are you trying to say here?

Response: “close from” was corrected to “close to”.

51. Page 10, line 306, This is interesting and should be better quantified. The term "better agreement" is too vague here.

Response: The statement is modified as follows (page 11, lines 328-331) :

If the absorption cross section from another publication (Brust et al., 2000) was used to retrieve HONO concentration, all HONO concentrations in IBBCEAS will increase 23%, which equal to multiply a factor of 1.23 to the currently presented HONO concentrations in Fig. 8(a). In this case, good agreement (with a linear-fit slope approaching 1) is observed between the HONO concentrations measured by LED-IBBCEAS and NitroMAC, respectively.

52. Page 10, line 311, “<5%”, The correlation is expressed through the slope and should be stated in that way.

Response: The related sentence was revised as follows (page 11, lines 332-335) :

The correlation and the regression analysis for the comparison between the FTIR and the IBBCEAS (2rd-4th peaks) is given in Fig. 8(c), displaying a slope of 0.952 with a y-axis intercept of 0.250 ppbv and a r^2=0.89. HONO-concentration variation profile (2rd-4th peaks in Fig. 8(a)) coincides well with each other between IBBCEAS and FTIR with a correlation slope close to 1. The discrepancy (<5%) is mainly due to the larger measurement uncertainty of HONO by FTIR.

53. Page 11, lines 327-328, “nm is not the highest for its sensitive measurement.”, rephrase. State a value or make this more quantitative in another way.

Response: revised as (page 12, line 351) "the corresponding CH_2O absorption cross section near 350 nm is not the maximal value in this region for its sensitive measurement".

54. Page 11, lines 331-332, ”offers the ability of self-calibration”, This needs re-phrasing. What is meant here by self-calibration.

Response: "offers the ability of self-calibration" is revised as (page 12, line 355-356) "offers the ability of self-calibration based on unique wavelength-dependent specific absorption intensity of the target molecules".

55. Page 11, line 333, An aspect not addressed in this paper, is the "interference" of aerosol on the retrieval. Fast changing aerosol concentrations (<2 min) are the biggest challenge for spectroscopic detection methods, especially in the near UV. For formaldehyde the influence of aerosol would strongly impinge on the quality of that data. This aspect should at least be mentioned when potential detection limits for other light sources are estimated. I understand that the influence of aerosol on the retrieval was not subject of this study, however, that is progress would have most scientific and/or technological merit.

Response: The following revised statement is provided to address aerosol interference issue (page 12, line 358-366) :

The present work in an atmospheric simulation chamber, with excellent measurements correlation on NO_2, HONO and CH_2O between IBBCEAS and other well-established instruments, shows that the IBBCEAS technique offers the ability of self-calibration for simultaneously measuring concentrations of these three species with high precision without significant interference influence even if their absorption cross sections are overlapped. For its application to an uncontrolled environment, the interference resulting from the presence of aerosols, in particular, would degrade the performance of the IBBCEAS measurement which is an issue to be carefully addressed. Under harsh environmental conditions, additional approaches, such as purging high-reflectivity mirror, using particle filter to reduce aerosol absorption and scattering, could be associated to extend the IBBCEAS technique to field campaign (Wu et al., 2014; Duan et al., 2018; Jordan et al., 2020).

56. Page 11, line 335, A uniform way of addressing formaldehyde should be used throughout the manuscript: H2CO, CH2O, HCHO

Response: Corrected, we used the uniform way of “CH_2O” for formaldehyde.

57. Page 11, line 338, “intercomparison of all instruments were found to be in good agreement”, "the intercomparison" itself is not in good agreement, but "the data" are in good agreement.

Response: This sentence was revised to (page 12, line 372-373) “The intercomparison of the measured data shows a good agreement on the temporal trends and variability in HONO, NO_2 and CH_2O.”

58. Page 11, line 340, “systematic bias”, Systematic errors were mentioned in correlation analysis.

Response: Agree with reviewer, “systematic bias” and the whole sentences (Exception of measurements near instrument detection limits, no evidence was found for any systematic bias in any of the instruments) was deleted.

59. Page 11, line 341, “positive”, positive?

Response: “positive” means “overestimation” (Villena et al., 2012).

60. Page 11, line 342, English

Response: This sentence was revised to (page 13, line 375) “Due to positive interference, NO_2 concentration measured using NOx analyzer was corrected by deduction of HONO contribution”

61. Page 12, line 351, “measurements spatially relevant”, “sounded volume.”, what are you trying to say? probed?

Response: “measurements spatially relevant of sounded volume” has been modified to (page 13, line 384) “measurements that spatially depends on the probed volume”.

62. Page 12, line 354, “without interference influence”, This statement is much too strong. Of course there are issues surrounding IBBCEAS and aerosol were not even considered. 2 sentences. It also has .

Response: “without interference influence” was deleted ("high-precision" is enough). The statements have been made in 2 sentences.

63. Page 12, line 357, “self-calibration”, ?? Not sure what is meant here.

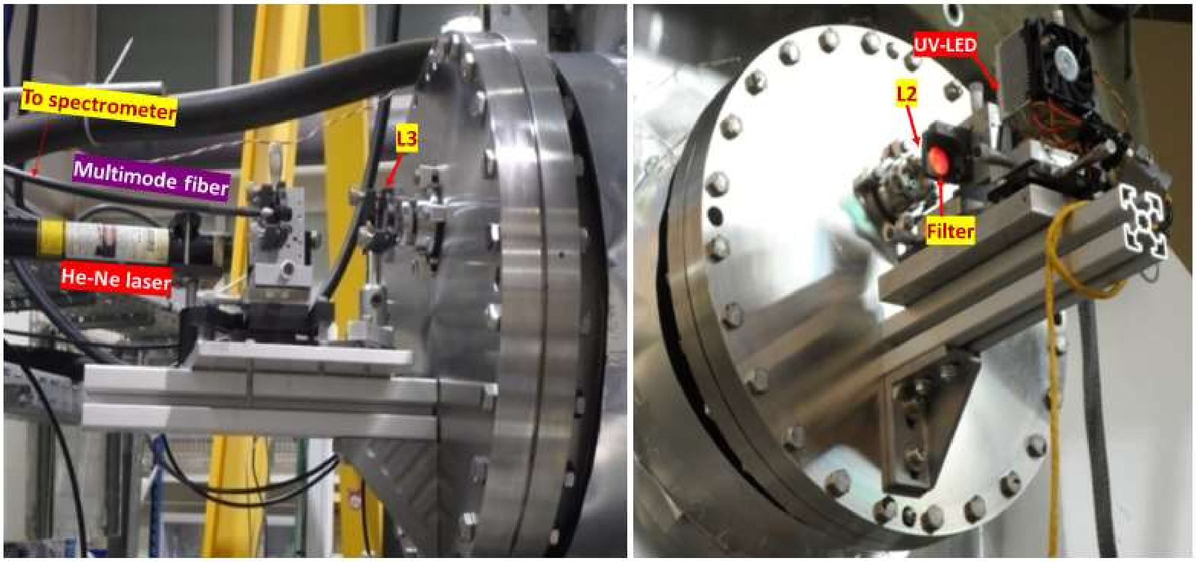
Response: as stated in the MS (page 12 lines 355-356): the term "self-calibrations" is conventionally used in optical sensor that measures light absorption by the target molecule to infer the concentration using its specific absorption line intensity ("self-calibrations"), in comparison to the needs of complicated calibration process using "external" chemical solutions for wet chemistry-based analytical instrument.

64. Page 19, line 546, what is L2 and L3. Divergence of the LED. FTIR pathway not well shown. The photograph has no explanations in it. The mirrors are not labelled, the size is not mentioned ... The figure can be strongly improved.

Response : Figure 1 has been updated according to reviewers’ suggestion, the following information has been added in the figure caption in the revised MS (page 21, lines 610-613): “Insert display a photograph of the set-up (left-top) and a schematic view from the top showing the angle between the two in-situ spectrometric pathways (left-bottom). L2 and L3 are BK7 achromatic focus lens. Cavity mirrors had 25 mm in diameter, 2 m radius of curvature and 6.35 mm thickness.”.

65. Page 19, line 551, No labels in figure 2. What is what? Where is the spectrometer?

Response: New labels have been added into the new figure as below:



66. Page 21, line 554, Is the shape of the LED spectrum real, or is it affected by some optical filters? Is the top of the LED spectrum really flat or is the spectrometer saturating? Were the zero air cross-sections measured or are they cited cross-sections from the literature? If the latter is the case the reference should be given?

Response: The shape of the LED emission is the real measurement result from a spectrometer, which is not affected by any optical filters and did not have any saturation of the spectrometer.

A reference (Miles et al., 2001) (Figure caption in figure 3) is provided into the revised manuscript for the used zero air cross-sections.

67. Page 21, line 557, The cross-section references should be cited here also.

Response: Reference of Miles et al. (2001) has been added in the revised manuscript (page 2, line 622).

68. Page 22, line 560, Too little information in the caption. What does "decomposed NO_2" and "decomposed HONO" mean? What measurements does this refer to?

Response: Decomposed NO_2 ($n_{NO_2} \cdot \sigma_{NO_2}(\lambda)$), HONO ($n_{HONO} \cdot \sigma_{HONO}(\lambda)$) and CH_2O ($n_{CH_2O} \cdot \sigma_{CH_2O}(\lambda)$) spectra are provided to show their individual contribution to the experimentally measured unique spectrum (Kennedy et al., 2011), which can be obtained from the fit using Eq. 3:

$$\alpha(\lambda) = n_{NO_2} \cdot \sigma_{NO_2}(\lambda) + n_{HONO} \cdot \sigma_{HONO}(\lambda) + n_{CH_2O} \cdot \sigma_{CH_2O}(\lambda) + a\lambda^2 + b\lambda + c$$

The following statement has been added to the revised manuscript (page 8, lines 239-241):

"In order to well show individual absorption of each molecule, the decomposed spectra (Kennedy et al., 2011) associated with the corresponding fit for NO_2, HONO and CH_2O are shown in Fig. 4(a) (blue line), Fig. 4(b) (black line), and Fig. 4(b) (green line), respectively."

69. Page 23, figure 5, Is there an explanation why a minimum is not reached? Is the system so incredibly stable? This should be by volume, i.e. ppbv. Same on the other axis. axis labelling not uniform. ->

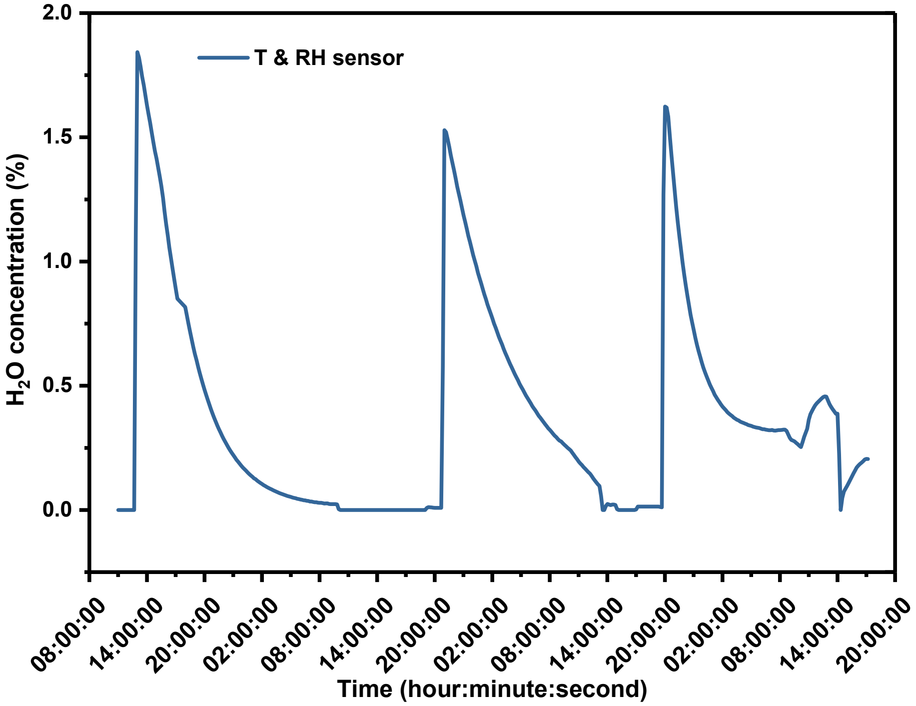
0.001. Typo in axis title! The green dashed line, being the chosen integration time, is not included here.

Response: "Typical Allan variance curves are plotted in Fig. 5, illustrating a highly desired white noise dominated system stability. As a compromise between detection limit (requiring long integration time) and measurement time response (requiring short measurement time), an integration time of 120 s was selected for use in the present work, which correspond to the measurement precision of 100 pptv for NO_2, 30 pptv for HONO and 40 ppbv for CH_2O."

The axis labelling and unit (ppbv) and typo on axis title were all corrected.

70. Page 24, figure 6, why are the "decays times" (wall loss rates) different between different injections of NO_2? what happened here?

Response: Because the introduced H_2O vapor and NO_2 concentrations (Figure 6) are all different at each injection. Please check the H_2O vapor concentration tracked by T&RH sensor in the following figure.



The following sentence is added in the revised manuscript (page 9, lines 271-272): "The peak concentrations of H_2O vapor, measured by the T&RH sensor, were 1.85%, 1.50% and 1.65% for 2nd to 4th peaks, respectively."

71. Page 25, figure 7, 1). ppbv. 2). I would call this "Time" rather than "Date". 3). ppbv on all axes. 4). CL NOx analyzer not applied uniformly throughout the manuscript.

Response: All these points have been corrected.

72. Page 26, figure 8(c), I take it that the IBBCEAS error bars are not missing but are within the size of the symbol. Is the difference in error really that large at 10 s of ppbv of HONO? In relative terms this is possible. In absolute terms the FTIR was used to calibrate the mirror reflectivity. The absolute uncertainty should not be better than what the calibration delivered, which is limited by the FTIR.

Response: Agree with the reviewer: absolute NO_2 concentrations measured by FTIR were used to calibrate mirror reflectivity, the uncertainty in NO_2 concentration related to the FTIR measurements would be transferred to the concentration measurement of HONO, NO_2 and CH_2O by IBBCEAS. We therefore improved the averaged times to about 100 scans (5 mins) to determine the mirror reflectivity so as to decrease the measurement uncertainty to about 7%.

73. All other issues referred to grammar, typo or English usage highlighted by blue symbols in the MS have been revised according to the reviewer's comments.