Response to Referees
Manuscript Number: amt-2016-319
Manuscript Title: Development of a portable Cavity Enhanced Absorption Spectrometer for the measurement of ambient $\text{N}_2\text{O}_5$: experimental setup, lab characterizations, and field applications under polluted urban environment

The discussion below includes the complete text from the referees, along with our responses to the specific comments and the corresponding changes made to the revised manuscript.

The detailed answers to the individual referee’s comments in blue.
All of the line numbers refer to the original manuscript.

Response to Referee #1 Comments:

We would like to thank the referee for his/her detailed comments and suggestions which helped us a lot to improve the quality of the paper. Our revised manuscript has been further edited by professional language services.

1. The manuscript of Wang et al., which reports on their new instrument to measure $\text{N}_2\text{O}_5$ is difficult to read. The level of English language is inadequate and only someone very close to this sort of instrument and its operation will make sense (after several readings) of some passages of text. The manuscript offers little that can be considered more than repetition of that which is already found in the literature for similar instruments. There is no “significant” design innovation and indeed the use of just one cavity to measure the sum of NO$_3$ and N$_2$O$_5$ means that this instrument can only be operated under high NOx (or low temperature) conditions when the NO$_3$-to-N$_2$O$_5$ ratio is likely to be low.

Answer:
We agree with the referee that we need to better differentiate our instruments to previous ones. To our knowledge, there were only two other field deployable CEAS instruments which had been reported before. One is a LED based CEAS system from the Cambridge University group (Langridge et al., 2008; Benton et al., 2010; Kennedy et al., 2011) and the other is a laser based CEAS system which is an optional mode of a CRDS system from the Max Planck Institute of Chemistry group (Schuster et al., 2009; Crowley et al., 2010). Our system is also a LED based CEAS system. To make it field deployable, the instrument is featured with a novel non-adjustable mechanically aligned mirror mounts (the concentricity error < 0.01°), see added Fig. 1b and Fig. 1c. The cavity is coupled automatically after we installed the HR mirrors into the mirror mounts and it reduces the background drift (e.g. thermal drift of the mechanics) significantly. The instrument is also featured with the addition of a chemical titration module which set up a dynamic reference spectrum for enhancing the precision of the spectrum fitting (e.g. the effects of the non-linear absorption lines of the water vapor is removed, the drift of the light power is eliminated). The chemical titration method has been widely used in the CRDS method for the determination of its zero point, but this is first time to be used in the CEAS type of instrument.

We agree that the amount of NO$_3$ detected in our instrument is the sum of NO$_3$ and N$_2$O$_5$ in general and represents N$_2$O$_5$ under high NOx (or low temperature) conditions. We changed the
term $N_2O_5$ to be $NO_{3X}$ ($NO_{3X} = NO_3 + N_2O_5$) throughout the manuscript, the later one was referred to Stone et al., (2014).

Figure 1. A schematic plot of the newly developed IBBCEAS instrument for the detection of $NO_{3X}$. (a) overview of the optical layout (LEDs, collimating optics, high-finesse cavity, and spectrometer) and the flow system (aerosol filter, inlet, $NO$ titration module, preheating tube, and detection cell). (b) the schematic layout of the mirror mounts, which enables a mechanical alignment of the high reflectivity (HR) mirrors. (c) a photograph of the mirror mounts. (d) the schematic layout of the $NO$ titration module; the red arrow denotes the $N_2$ gas flow, and the blue arrow denotes the $NO$ gas flow.

2. The instrument is described as small and portable, yet no information about its weight or size (or power consumption) or given. No useful comparison is made to existing devices that measure $N_2O_5$. The manuscript is not suitable for publication in AMT. The following comments may help the authors should they consider re-writing. They should also seek assistance in improving the English.

Answer:
In the first graph of Sect. 2, we added a brief introduction as the followings:
“The total weight is less than 25 kg, approximate dimensions of 95×40×25 cm, the power consumption is less than 300 W.”
We added a revised Table 3 in which a detailed comparison of the LOD and uncertainty with the existing field devices is presented (see also our answers to question 6.).
3. L25. Why do high levels of N₂O₅ imply an active nighttime chemistry? If N₂O₅ builds up it may in part be due to lack of reactivity of NO₃ or lack of uptake of N₂O₅ to aerosol.

**Answer:**
The high levels of NO₃X were observed in parallel with the presence of high aerosol loadings so that an active nighttime chemistry is implied.
We revised the sentence as: “Up to 1.0 ppb NO₃X were observed with the presence of high aerosol loadings which indicates an active nighttime chemistry running in Beijing.”

4. L64. CEAS is suggested to give better selectivity that CRDS. Can the authors give an example of when CRDS measurements of NO₃ are not specific?

**Answer:**
We agree with the referee. Both the CEAS and CRDS are suitable to detect NO₃/N₂O₅ with high selectivity. We removed this statement. In the past, we mean that CEAS measured the absorption spectrum with a wavelength window while CRDS observed cavity decay time caused by the molecules absorption at a specific wavelength.

5. L70. Vertical profiles of NO₃ are suggested to be important. This is undoubtable the case, but why is it mentioned here? is the instrument designed for or suitable for airborne operation (weight, power, size)?

**Answer:**
The instrument is designed with the feature of small size and low power consumptions which potentially meet the future applications on the mobile platforms for the vertical profile measurement. We revised the text accordingly.
We added the information about the weight, power and size in the first graph of Sect. 2 as suggested (see also our answers to question 2).

6. L90. Compare this instrument with the IBBCEAS already in operation (Langridge, Benton, Kennedy)? Compare LOD and uncertainty with other N₂O₅ detection methods.

**Answer:**
We compared the LOD and uncertainty with other field NO₃ and N₂O₅ detection systems in Sect. 4.4 and Table 3 in the revised text as “The LOD and the uncertainty of the existing field measurement techniques of NO₃ and N₂O₅ (NO₃X) are listed in Table 3. For the NO₃ measurement, CRDS, CEAS and LIF are available with the LOD of 0.2 - 10 ppt and the uncertainties lower than 25%; for the N₂O₅ measurement, the three methods mentioned above and CIMS are available with the LOD of 0.5-12 ppt and the uncertainties lower than 40%.”

**Table 3.** Limits of detection (LOD) and uncertainty of the existing field deployable instruments of NO₃ and N₂O₅ (NO₃X).

<table>
<thead>
<tr>
<th>Method</th>
<th>NO₃ LOD</th>
<th>NO₃ Uncertainty</th>
<th>N₂O₅ (NO₃X) LOD</th>
<th>N₂O₅ (NO₃X) Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>CEAS</td>
<td>2.4 pptv (1s)</td>
<td>19% - 22%</td>
<td></td>
</tr>
<tr>
<td>Kennedy et al., 2011</td>
<td>CEAS</td>
<td>1.1 pptv (1s)</td>
<td>11%</td>
<td>2.4 pptv (1s)</td>
</tr>
<tr>
<td>Bitter et al., 2005</td>
<td>CEAS</td>
<td>1 pptv (100s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


7. **L148. Coated stand steel tube (stainless?)**

   **Answer:** We revised the “Coated stand steel tube” as “coated stainless tube”

8. **L187. “N₂O₅ is normally two orders of magnitude small concentrated than NO₂ during nighttime. This is not true. There are plenty of examples where N₂O₅ is a substantial fraction of NOx. Also, N₂O₅ (and thus the NO₃ formed can be close to zero at night (as the authors show in their own data). When N₂O₅ is close to zero, the NO₃ formed by thermal dissociation is then not the dominant absorber.**

   **Answer:**
   We agree with the referee and this assumption is actually not required in our data analysis. We deleted this sentence.

9. **L195. How was the d_{eff} established to be 45.0 cm using NO₂? Was this a bottled standard of NO₂? What is the uncertainty of this approach (bottled mixing ratios, NO₂ cross sections)?**

   **Answer:**
   We supplied a NO₂ gas standard (200 ppb) with a constant flow into the cavity and then retrieved the d_{eff} based on Eq. 1 in the text. The NO₂ gas standard was delivered from a bottled standard of NO₂ and diluted by synthetic air with a gas calibrator (TE-146i). The measured NO₂ concentration by switching off the purge flow was in good agreement with the delivered NO₂ gas standard (within 2%). The uncertainty of the NO₂ standard is estimated to be 2%, the uncertainty of the NO₂ cross section is estimated to be 4.7 % according to Voigt et al. (2002) and the associated uncertainty of the determined d_{eff} with this approach is about 5%.

10. **L237. “The excess NO is sufficient to chemically destroy (destruct) the ……..NO₃.” What was the NO mixing ratio, show the calculation. What was the NO₂ impurity in the NO bottle?**

    **Answer:**
    When NO injection is performed, the NO mixing ratio resulted in the sample gas flow is 480 ppb and the NO₂ impurity in the NO bottle is determined to be 0.8%. In the revised Sect. 2.3 “Dynamic reference spectrum”, we addressed this issue as follows:

    “The NO titration module is connected to the inlet tube by a PFA tee-piece. Using a computer controlled solenoid valve, the instrument measures reference and sampling spectrums

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Concentration</th>
<th>Absorption</th>
<th>Time</th>
<th>Duplicated Concentration</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schuster et al., 2009</td>
<td>CRDS/CEAS</td>
<td>2 pptv (5s)</td>
<td>14 %</td>
<td></td>
<td>2 pptv (5s)</td>
<td>13 %</td>
</tr>
<tr>
<td>Nakayama et al., 2008</td>
<td>CRDS</td>
<td>1.5 pptv (100s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dube et al., 2006</td>
<td>CRDS</td>
<td>0.2 pptv (1s)</td>
<td>25 %</td>
<td></td>
<td>0.5 pptv (1s)</td>
<td>20 % - 40 %</td>
</tr>
<tr>
<td>Ayers et al., 2005</td>
<td>CRDS</td>
<td>2 pptv (25s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang et al., 2015</td>
<td>CRDS</td>
<td>3.2 pptv (10s)</td>
<td>8 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matsumoto et al., 2006</td>
<td>LIF</td>
<td>10 pptv (600s)</td>
<td>17 %</td>
<td></td>
<td>12 pptv (600s)</td>
<td>17 %</td>
</tr>
<tr>
<td>Slusher et al., 2004</td>
<td>CIMS</td>
<td></td>
<td></td>
<td></td>
<td>2.7 pptv (60s)</td>
<td>20 %</td>
</tr>
<tr>
<td>Kercher et al., 2009</td>
<td>CIMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang et al., 2016</td>
<td>CIMS</td>
<td>4 pptv (60s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sequentially by switching the NO injection on and off (NO = 98 ppmv, flow rate = 10 ml/min). A high purity N₂ line (OD = 3.175 mm) is added at the exit of the solenoid valve by a PFA tee-piece to flush the residual NO after the NO injection is switched off (Fig. 1d). The resulting NO mixing ratio is about 480 ppbv in the sample flow when NO injection is performed. Since 8.0 ppb N₂O₅ was once observed and reported in Hong Kong (Wang et al., 2016) as an extreme case, the ambient NO₃, N₂O₅, and O₃ were set at about 1 ppbv, 10 ppbv, and 100 ppbv, respectively, for the simulation, proving that the ambient NO₃ and N₂O₅ can be removed within a time scale of 0.05 s when NO is injected (Fig. 2).

The NO₂ impurity in the used NO standard is analysed by a commercial NOx instrument (TE-42i). The NO₂ impurity is found to be around 0.8 %, which means 4 ppbv of NO₂ is present in the reference spectrum measurement with the presence of 480 ppbv NO. The NO₃ and O₃ in the preheating tube and detection cell react with the high concentration of NO and generate NO₂. In the case shown as Fig. 2, the additional NO₂ produced during the measurement of the reference spectrum can reach up to 55 ppb (with the initial additional NO₂ set at 4 ppb). Therefore, to use this dynamic reference spectrum, we normally fit both NO₃ and NO₂ to cover the limiting cases when the generated NO₂ is high. Nevertheless, the fitted NO₂ concentration will be negative since the NO₂ concentrations are higher in the reference spectrum.

![Figure 2](image)

**Figure 2.** Simulation of the change of the mixing ratios of NO₃, N₂O₅ and NO₂ during the NO titration mode in the preheating tube and detection cell for an extremely high NO₃ and N₂O₅ case. The initial ambient NO₃, N₂O₅ and O₃ were set at 1 ppb, 10 ppb and 100 ppb, respectively. The initial NO₂ was set at 4 ppb from the impurity of the used NO standard.

11. L295-313. The whole section is confusing. Some points: The purge flow does not result in a dilution of the NO₃. It flushes the NO₃ through the cavity changing the optical path length. This requires a different calculation to make the correction. Stopping the flow to measure NO₃ loss in the cavity will mean that you lose information about point losses in front of the cavity (i.e. at mixing points in the tubing). Show the calculations to derive the effective transmission from the measurements of wall loss and residence time.
The impact of the purge flow on the calculated NO\textsubscript{3} wall loss reactivity is now corrected through a view of changed optical path length.

The corresponding text is revised as follows:

“To determine the wall loss reactivity of NO\textsubscript{3}, the heated detection cell is used as a flow tube. Gas samples with a stable amount of N\textsubscript{2}O\textsubscript{5} are delivered by the NO\textsubscript{3}/N\textsubscript{2}O\textsubscript{5} source described above. By stopping the sample gas flow, the observed NO\textsubscript{3} versus the elapsed time determines the first order loss rate of NO\textsubscript{3} in the heated detection cell. In this experiment, the fitted first order uptake coefficient of NO\textsubscript{3} reflects the contribution from three processes: (1) the wall loss of the NO\textsubscript{3} in the detection cell; (2) the change of the effective cavity length due to the adding of the purge flows; and (3) the production of NO\textsubscript{3} from the reaction of NO\textsubscript{2} and O\textsubscript{3}. The NO\textsubscript{2} concentration determined in the running sampling gas flow is used to determine the change of \(d_{\text{eff}}\) corresponding to the elapsed time after stopping the sample flow (in the way it is used to quantify the \(d_{\text{eff}}\) in Sect. 3.3). A time series of \(d_{\text{eff}}\) is determined with high time resolution data acquisition (0.5 s) that is then used to quantify the mixing ratio of NO\textsubscript{3} in the corresponding time intervals. Figure 7 shows the decay of the observed NO\textsubscript{3} concentrations versus the elapsed time on a logarithmic scale. The fitted first order decay rate is \(0.13 \pm 0.02\ \text{s}^{-1}\) with a good correlation coefficient \(R^2=0.991\). Finally, the fitted first order decay rate is corrected by the chemistry of R1 and R4 with a box model constrained to observed NO\textsubscript{2} and O\textsubscript{3}. The NO\textsubscript{3} wall reactivity of the heated detection cell surface is determined to \(0.16 \pm 0.02\ \text{s}^{-1}\), which is similar to previous results of \(0.1–0.3\ \text{s}^{-1}\) (Brown et al., 2002; Crowley et al. 2010; Kennedy et al. 2011; Wang et al., 2015).”

The detailed calculations to derive the transmission efficiency of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are now listed as Table 1 in the revised manuscript. As reported by Kennedy et al., (2011), the NO\textsubscript{3} wall loss reactivity in the cold PFA piping (inlet) is the same as the heated ones with the value of \(0.27\ \text{s}^{-1}\). Nevertheless, we noticed that Crowley et al. (2010) reported that the NO\textsubscript{3} wall loss reactivity of the cold PFA tube could be a factor of two larger than that of the heated tube. We thus assumed our NO\textsubscript{3} wall loss reactivity for the cold PFA tube is between \(0.16\ \text{s}^{-1}\) and \(0.32\ \text{s}^{-1}\) and on average NO\textsubscript{3} wall loss reactivity for the cold PFA tube is estimated to be \(0.24\ \text{s}^{-1}\) with an uncertainty of \(0.06\ \text{s}^{-1}\).

12. L311. How was the total transmission efficiency of NO\textsubscript{3} derived? What is the loss rate constant in cold PFA piping (the inlet)?

The detailed calculations to derive the total transmission efficiency of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are now listed as Table 1 in the revised manuscript.

As reported by Kennedy et al., (2011), the NO\textsubscript{3} wall loss reactivity in the cold PFA piping (inlet) is the same as the heated ones with the value of \(0.27\ \text{s}^{-1}\). Nevertheless, we noticed that Crowley et al. (2010) reported that the NO\textsubscript{3} wall loss reactivity of the cold PFA tube could be a factor of two larger than that of the heated tube. We thus assumed our NO\textsubscript{3} wall loss reactivity for the cold PFA tube is between \(0.16\ \text{s}^{-1}\) and \(0.32\ \text{s}^{-1}\) and on average NO\textsubscript{3} wall loss reactivity for the cold PFA tube is estimated to be \(0.24\ \text{s}^{-1}\) with an uncertainty of \(0.06\ \text{s}^{-1}\).

Table 1. The transmission efficiency of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} for the sampling module setup for the developed instrument.
Gases | Filter | Inlet tube (0.7 s) | Preheating tube (0.14 s) | Cavity (0.46 s) | Total
--- | --- | --- | --- | --- | ---
NO$_3$ | 72±3 %$^a$ | 84±4 % (k=0.24 s$^{-1}$)$^b$ | 98 % (k=0.16 s$^{-1}$)$^b$ | 93 % (k=0.16 s$^{-1}$)$^b$ | 55±6 %
N$_2$O$_5$ | 93±3 %$^a$ | 99 % (k=0.019 s$^{-1}$)$^c$ | 99±1 %$^c$ | 93 % (k=0.16 s$^{-1}$)$^c$ | 85±3 %

Note: $^a$ filter aging contributed an uncertainty of 3 %; $^b$ the uncertainty of the NO$_3$ wall loss reactivity in the cold inlet tube caused an uncertainty of 4 %; $^c$ the location of the N$_2$O$_5$ dissociation in the preheating tube had an uncertainty of 1 %.

13. L320. Explain how the best limit of detection was derived. Was it taken from the intersection of the two dotted lines? Why should this give the best detection limit?

**Answer:**
We first used the Allan deviation plot to determine the best integration time and then analyzed the standard deviation of our measurement results for synthetic air at such integration time interval. According to the Allan variance approach, the best integration time appeared at the intersection of the white noise and the fitted drift (e.g. Fig. 6 of Langridge et al., 2008; Fig. 8 of Min et al., 2016).

14. L324. The total uncertainty on the scattering cross sections of He and N$_2$ is given as 5 %. Where does this number come from? Any significant difference between N$_2$ and air?

**Answer:**
The total uncertainty on the scattering cross sections of N$_2$ is about 5% according to Sneep and Ubachs (2005) and the uncertainty for He makes a negligible contribution (Washenfelder et al., 2008). No significant difference is between N$_2$ and air, therefore air and He is also used to determine the mirror reflectivity during field studies (e.g. Min et al., 2016).

15. L344. What were the “conditions experienced for the winter campaign” that ensure that N$_2$O$_5$ / NO$_3$ is greater than 10?

**Answer:**
In the winter campaign, the averaged nighttime temperature and NO$_2$ mixing ratio were -4.3 °C and 15.5 ppb, respectively; the calculated ratio of N$_2$O$_5$ and NO$_3$ based on a box model was larger than 100.

16. L355. The presence of HDV results in loss of N$_2$O$_5$. Provide (and justify) a hypothesis why this is the case.

**Answer:**
It is known that HDV would emit large amount of fresh NO. The emitted NO will titrate both O$_3$ and NO$_3$ and reduce the accumulation of N$_2$O$_5$ (NO$_3$+NO$_2$→N$_2$O$_5$) or enhance the loss of N$_2$O$_5$ (N$_2$O$_5$→NO$_3$+NO$_2$) in the time scale of N$_2$O$_5$ thermal dissociation (0.1 – 20 min from summer to winter).

17. L364. What is meant by “a steady state calculation”? Is this referring thermodynamic equilibrium between NO$_2$, NO$_3$ and N$_2$O$_5$?

**Answer:**
Yes, “a steady state calculation” refers to the thermodynamic equilibrium between NO$_2$, NO$_3$
and N\textsubscript{2}O\textsubscript{3}. We modified the text accordingly.