Response to Referees

Manuscript Number: amt-2016-319

Manuscript Title: Development of a portable Cavity Enhanced Absorption Spectrometer for the measurement of ambient N_2O_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 N_2O_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_2O_5 means that this instrument can only be operated under high NOx (or low temperature) conditions when the NO_3-to-N_2O_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 $< 0.01^\circ$), 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_2O_5 in general and represents N_2O_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).
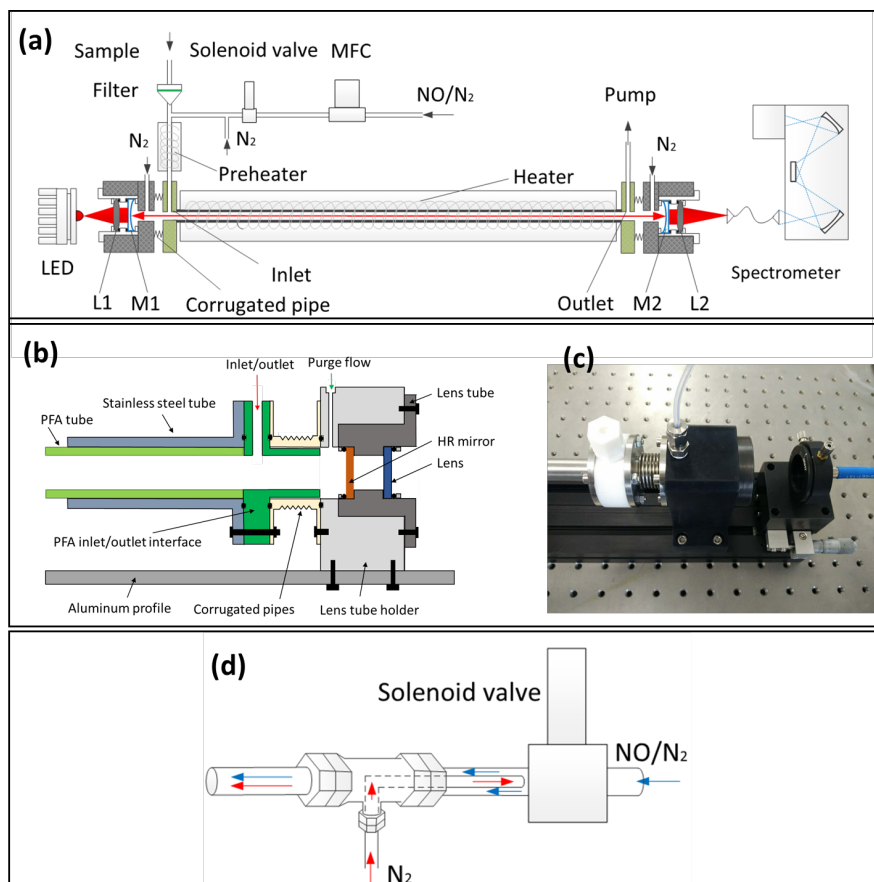
Figure 1. A schematic plot of the newly developed IBBCEAS instrument for the detection of NO_{3X}. **(a)** overview of the optical layout (LEDs, collimating optics, high-finesse cavity, and spectrometer) and the flow system (aerosol filter, inlet, NO titration module, preheating tube, and detection cell). **(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 N2 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 N_2O_5 imply an active nighttime chemistry ? If N_2O_5 builds up it may in part be due to lack of reactivity of NO_3 or lack of uptake of N_2O_5 to aerosol.
   Answer:
   The high levels of NO_{3X} 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 NO_{3X} 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 NO_3 are not specific. ?
   Answer:
   We agree with the referee. Both the CEAS and CRDS are suitable to detect NO_3/N_2O_5 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 NO_3 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 N_2O_5 detection methods.
   Answer:
   We compared the LOD and uncertainty with other field NO_3 and N_2O_5 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 NO_3 and N_2O_5 (NO_{3X}) are listed in Table 3. For the NO_3 measurement, CRDS, CEAS and LIF are available with the LOD of 0.2 - 10 ppt and the uncertainties lower than 25%; for the N_2O_5 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 NO_3 and N_2O_5 (NO_{3X}).

	Method	NO_3		N_2O_5 (NO_{3X})	
		LOD	Uncertainty	LOD	Uncertainty
This work	CEAS			2.4 pptv (1s)	19% - 22 %
Kennedy et al., 2011	CEAS	1.1 pptv (1s)	11 %	2.4 pptv (1s)	14 %
Bitter et al., 2005	CEAS	1 pptv (100s)			

Schuster et al., 2009	CRDS/ CEAS	2 pptv (5s)	14 %	2 pptv (5s)	13 %
Nakayama et al., 2008	CRDS	1.5 pptv (100s)			
Dube et al., 2006	CRDS	0.2 pptv (1s)	25 %	0.5pptv (1s)	20 % - 40 %
Ayers et al., 2005	CRDS	2 pptv (25s)			
Wang et al., 2015	CRDS	3.2 pptv (10s)	8 %		
Matsumoto et al., 2006	LIF	10 pptv (600s)	17 %	12 pptv (600s)	17 %
Slusher et al., 2004	CIMS			12 pptv (1s)	
Kercher et al., 2009	CIMS			2.7 pptv (60s)	20 %
Wang et al., 2016	CIMS			4 pptv (60s)	20 %

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

Answer: We revised the "Coated stand steel tube" as "coated stainless tube"

8. L187. "N_2O_5 is normally two orders of magnitude small concentrated than NO_2 during nighttime. This is not true. There are plenty of examples where N_2O_5 is a substantial fraction of NOx. Also, N_2O_5 (and thus the NO_3) formed can be close to zero at night (as the authors show in their own data). When N_2O_5 is close to zero, the NO_3 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 NO_2 ? Was this a bottled standard of NO_2. What is the uncertainty of this approach (bottled mixing ratios, NO_2 cross sections)?

Answer:

We supplied a NO_2 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 NO_2 gas standard was delivered from a bottled standard of NO_2 and diluted by synthetic air with a gas calibrator (TE-146i). The measured NO_2 concentration by switching off the purge flow was in good agreement with the delivered NO_2 gas standard (within 2%). The uncertainty of the NO_2 standard is estimated to be 2%, the uncertainty of the NO_2 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 …......NO_3." What was the NO mixing ratio, show the calculation. What was the NO_2 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 NO_2 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

sequentially by switching the NO injection on and off (NO = 98 ppmv, flow rate = 10 ml/min). A high purity N_2 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 N_2O_5 was once observed and reported in Hong Kong (Wang et al., 2016) as an extreme case, the ambient NO_3, N_2O_5, and O_3 were set at about 1 ppbv, 10 ppbv, and 100 ppbv, respectively, for the simulation, proving that the ambient NO_3 and N_2O_5 can be removed within a time scale of 0.05 s when NO is injected (Fig. 2).

The NO_2 impurity in the used NO standard is analysed by a commercial NOx instrument (TE-42i). The NO_2 impurity is found to be around 0.8 %, which means 4 ppbv of NO_2 is present in the reference spectrum measurement with the presence of 480 ppbv NO. The NO_3 and O_3 in the preheating tube and detection cell react with the high concentration of NO and generate NO_2. In the case shown as Fig. 2, the additional NO_2 produced during the measurement of the reference spectrum can reach up to 55 ppb (with the initial additional NO_2 set at 4 ppb). Therefore, to use this dynamic reference spectrum, we normally fit both NO_3 and NO_2 to cover the limiting cases when the generated NO_2 is high. Nevertheless, the fitted NO_2 concentration will be negative since the NO_2 concentrations are higher in the reference spectrum."
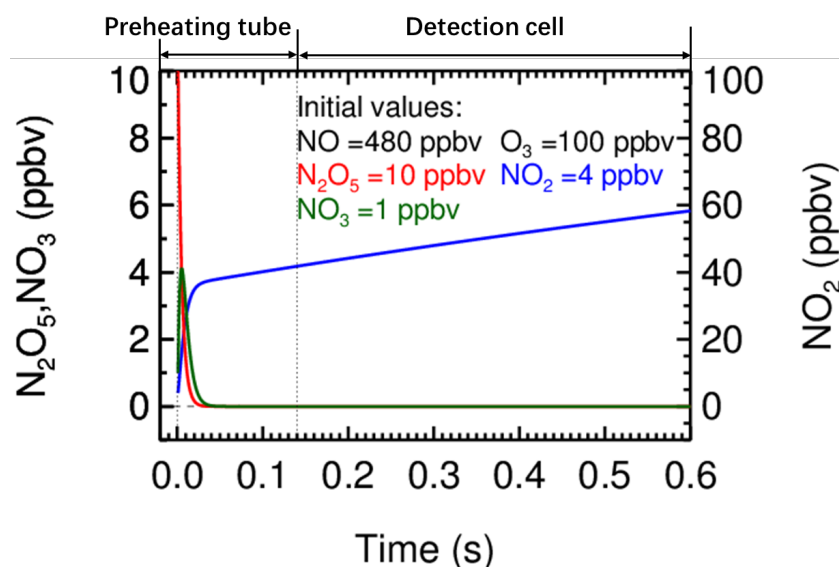
Figure 2. Simulation of the change of the mixing ratios of NO_3, N_2O_5 and NO_2 during the NO titration mode in the preheating tube and detection cell for an extremely high NO_3 and N_2O_5 case. The initial ambient NO_3, N_2O_5 and O_3 were set at 1 ppb, 10 ppb and 100 ppb, respectively. The initial NO_2 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 NO_3. It flushes the NO_3 through the cavity changing the optical path length. This requires a different calculation to make the correction. Stopping the flow to measure NO_3 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.

Answer:

The impact of the purge flow on the calculated NO_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_3, the heated detection cell is used as a flow tube. Gas samples with a stable amount of N_2O_5 are delivered by the NO_3/N_2O_5 source described above. By stopping the sample gas flow, the observed NO_3 versus the elapsed time determines the first order loss rate of NO_3 in the heated detection cell. In this experiment, the fitted first order uptake coefficient of NO_3 reflects the contribution from three processes: (1) the wall loss of the NO_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_3 from the reaction of NO_2 and O_3. The NO_2 concentration determined in the running sampling gas flow is used to determine the change of d_{eff} corresponding to the elapsed time after stopping the sample flow (in the way it is used to quantify the d_{eff} in Sect. 3.3). A time series of d_{eff} is determined with high time resolution data acquisition (0.5 s) that is then used to quantify the mixing ratio of NO_3 in the corresponding time intervals. Figure 7 shows the decay of the observed NO_3 concentrations versus the elapsed time on a logarithmic scale. The fitted first order decay rate is 0.13 ± 0.02 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_2 and O_3. The NO_3 wall reactivity of the heated detection cell surface is determined to 0.16 ± 0.02 s^{-1}, which is similar to previous results of 0.1–0.3 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_3 and N_2O_5 due to the wall losses and the residence time are referred to our answers to question 12.

The surface materials are the same of the inlet tube, the preheating tube and the detection cell. Therefore, to determine the wall loss reactivity of NO_3 in the detection cell shall then be applicable for the inlet and the preheating tubes (As shown in Fig. 1, our instrument had only one mixing point at the set up of the NO titration module. And there is no block of the main sample gas flow of the PFA tee-piece. Thus, we think the influence of mixing point could be neglected).

12. L311. How was the total transmission efficiency of NO_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_3 and N_2O_5 are now listed as Table1 in the revised manuscript.

    As reported by Kennedy et al., (2011), the NO_3 wall loss reactivity in the cold PFA piping (inlet) is the same as the heated ones with the value of 0.27 s^{-1}. Nevertheless, we noticed that Crowley et al. (2010) reported that the NO_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_3 wall loss reactivity for the cold PFA tube is between 0.16 s^{-1} and 0.32 s^{-1} and on average NO_3 wall loss reactivity for the cold PFA tube is estimated to be 0.24 s^{-1} with an uncertainty of 0.06 s^{-1}.

Table 1. The transmission efficiency of NO_3 and N_2O_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})	93 % ($k=0.16$ s^{-1})	55 ± 6 %
N_2O_5	93 ± 3 %[a]	99 % ($k=0.019$ s^{-1})	99 ± 1 %[c]	93 % ($k=0.16$ s^{-1})	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_2O_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_2O_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_2O_5 and NO_3 based on a box model was larger than 100.

16. L355. The presence of HDV results in loss of N_2O_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_2O_5 ($NO_3+NO_2\rightarrow N_2O_5$) or enhance the loss of N_2O_5 ($N_2O_5\rightarrow NO_3+NO_2$) in the time scale of N_2O_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_2O_5 ?

Answer:

Yes, "a steady state calculation" refers to the thermodynamic equilibrium between NO_2, NO_3

and N_2O_5. We modified the text accordingly.