Response to reviewers' comments on:

An Aircraft Based Three Channel Broadband Cavity Enhanced Absorption Spectrometer for Simultaneous Measurements of NO_3, N_2O_5 and NO_2

We thank both reviewers for their interest in the paper and for their helpful and constructive comments. This has now been included in the acknowledgements. Our responses are outlined in blue below together with the referees' comments which have been reproduced in black.

Anonymous referee #1

Page 3506, line 26. Briefly describe the need for such a large flow rate.

The following sentence has been added to the text (on Page 3506, line 26):

"The purpose of such large flow rates is to minimise the sample residence time of each channel and thus to reduce the wall losses of N_2O_5 and NO_3, as is described in more detail in Sect. 3.

Page 3507, line 3. Dissociation efficiency of N2O5 is 100% - does the model take into account the time required to heat the gas sample, in addition to the time required to dissociate N2O5?

Yes. This has been clarified in the text, which now reads:

"A modelling study simulating the flow conditions (i.e. flow rates, flow line geometries etc.) gave dissociation efficiencies of N_2O_5 greater than 99.6% for a range of inlet air temperatures (-20 to 20 °C) and NO_2 concentrations (2 to 60 ppb). The expectation is that the efficiency is therefore sufficiently close to unity c.f. other sources of error (as is detailed in Sect.3) that 100% conversion efficiency is assumed."

Section 3.3: NO3 measurement accuracy. The error in T2 associated with NO3 transmission efficiency seems somewhat low. Since (if I have understood correctly) the calibration is based on offline measurements of NO3 wall loss in a stopped flow, the determined T2 does not account for the potential effect of larger wall loss if the tubing becomes contaminated during sampling. Some estimate of, or at least a discussion of, this potential effect would be helpful.

This is an important point. The loss experiments detailed in Sect. 3 of the paper were in fact performed before and after each instrument flight (the first flight was in December 2009 and the most recent flight was in January 2011). It was established in these experiments that $k_{NO3loss}$ was unchanged over this period. These details were omitted from the original manuscript but the following text has now been included in Sect. 3.1.1 for clarification:

"Note that changes to the PFA surface, in terms of its NO_3 uptake properties, caused by aging or build-up of particulates during sampling, were investigated by performing the stopped flow experiment (detailed above) before take off and after landing each time the instrument has flown on the BAe 146 aircraft (an overview of the flights completed by the instrument to date is given in Sect. 5). Thus far, the measured $k_{NO3loss}$ rate coefficient has been, in each case, within the error of that quoted above, indicating any such effects to be negligible."

Page 3518, line 21. Cite primary reference for Allan variance.

Reference cited

Page 3519, line 12: "Sensitivity is less than" Does this mean better (a smaller detection limit) or worse (a larger one)? Wording should be clearer. The discussion about sensitivity that follows is otherwise clear, however.

Less has been replaced with worse

Page 3519, line 16: Effect of aerosols on the spectral fitting procedure. Can the authors be more specific about the complications associated with fitting aerosol? Some comparison of the aerosol extinction to the other background cavity losses (e.g., mirror reflectivity, Rayleigh scattering) would be useful since it would seem that aerosol extinction could change the NO3 or NO2 retrieval if not accounted for properly.

Using BBCEAS (or CE-DOAS) for aerosol extinction measurements has been described previously in the literature and the text now explicitly directs the reader to two nice references for more details (Varma et al., 2009;Thalman and Volkamer, 2010) (Sect. 1.2). As was stated is stated in Sects. 1.1 and 1.2, the BBCEAS

spectral analysis procedure used in the present study, which involves quantification of molecular absorption rather than aerosol extinction, has been rigorously explained in previous publications (Ball et al., 2004;Langridge et al., 2008). In brief, this procedure is robust in terms of its ability to correctly retrieve NO_3 and NO_2 concentrations and, if required, aerosol extinction from BBCEAS extinction spectra, as long as variations in cavity throughput intensity are caused by intracavity optical extinction rather than mirror reflectivity changes or light source drifts (as neither are distinguished from smoothly varying intracavity attenuation mechanisms such as aerosol extinction). In the present instrument, this is indeed the case (i.e. that the method is robust), which can now be inferred from the following information that has been added to the text: Firstly, it is stated in Sect. 2,1 that reflectivity remains stable during flights on account of the nitrogen gas flowing into the volumes directly in front of each mirror surface; and secondly, in Sect. 2.2 it is detailed that measurements of I_0 (i.e. the spectrum when the cavity is flushed with nitrogen) are acquired with a periodicity of half an hour in order to account for light source drifts.

Figure 3: Figure is somewhat unclear. For example, there are two flow controllers labeled "MFC", but an arrow points at two other things that are labeled flow controllers. There is something strange and unlabeled in the bottom left corner of the figure. Where are temperature and pressure measured? Temperature and pressure measurements are also not mentioned in the text.
Figure 3 has been updated in response to these comments.
Pressure and temperature measurements are now mentioned explicitly in Sect 2; the relevant part now reads:
"The first inlet, inlet 1, is used for sampling ambient air while the second inlet, inlet 2, is used to draw ambient air through a sheath encompassing channel 2 (see table 1), which measures ambient NO_3 concentrations. The sheath flow maintains the temperature of channel 2 (the temperatures of the cavities are measured using PT1000 temperature sensors equally spaced along the cavity tubes) at ambient temperature. This minimises the potential for perturbation of the N_2O_5/NO_3 equilibrium due to heating of the sample as it enters the aircraft cabin. Note that the pressure inside the cavities is inferred from pressure sensors at the exhausts of conduits 1 and 2. During testing, the readings from these sensors were in excellent agreement with those reported by a pressure gauge when attached to 1/8 inch fittings on each of the instruments mirror mounts (i.e. those normally attached to the lines which bring the nitrogen gas used to purge the volume directly in front of each mirror face– see Sect. 2.1)."

Figure 10: The two NO3 fits should be more clearly labelled as belonging to different channels. Also, on the topic of spectral fitting, the authors provide good detail about the spectral fitting of narrow H2O absorption features. Besides that, there is no information about the spectral fitting. What software is used? Do the fits include any arbitrary offsets to account for lamp intensity variations? A short section describing fits would be helpful to the reader.
We agree that details of the DOAS fitting algorithm used in BBCEAS would potentially be interesting to the reader (note that we use in-house developed software). It is, however, detailed in the text that more information on the BBCEAS fitting procedure can be found in the references which have been updated to include Varma et al., (2009) and Thalman and Volkamer, (2010). In particular, the reader is directed to publications by Ball et al., (2004) and Langridge et al., (2008), where the BBCEAS fitting procedure is thoroughly described. Note that no arbitrary offsets are applied to account for lamp intensity variations.

Anonymous referee #2

The following two references should be added for further information:

1. Thalmann, Volkamer (http://www.atmos-meas-tech.net/3/1797/2010/amt-3-1797-2010.html) Shows a BBCEAS instrument measuring (amongst others) NO2, and also deals with aerosols. 2. Wagner, Brown, et al. (http://www.atmos-meas-tech.net/4/1227/2011/amt-4-1227-2011.html) Describes a CRDS Instrument measuring NO3, NO2, N2O5 on aircraft.

Reference 1 added in Sect. 1.2

Reference 2 added in Sect. 3

In general, information about pressure levels in the cavities is missing, as well as the measurement.

Following sentence has been added in to Sect 2.2

"Note that the pressure inside the cavities is inferred from pressure sensors at the exhausts of conduits 1 and 2. During testing, the readings from these sensors were in excellent agreement with those reported by a pressure gauge when attached to 1/8 inch fittings on each of the instruments mirror mounts (i.e. those normally attached to the lines which bring the nitrogen gas used to purge the volume directly in front of each mirror face– see Sect. 2.1)."

78: Replace "of some species" with a detailed information.

Sentence now reads:

"These gases are of interest due to their participation in a range of atmospheric processes: oxidation by NO_3 controls the lifetimes of some species, including certain volatile organic compounds (VOCs) that are important for photochemical ozone production, while deposition of N_2O_5 onto certain aerosol surfaces represents a potentially important but presently unquantified sink of diurnally aggregated NO_x (Chang et al., 2011)."

128: Is there a reason for using fibers? Couldn't one collimate the LEDs directly?

Following sentence has been added in to Sect 2.1

"Note that the use of fibre optics conveniently allows the LEDs to be mounted on a single thermo-electric cooler (TEC) inside an enclosure for temperature regulation"

162: N2O5/NO3 equilibrium is kept at a constant temperature in channel 2. Isn't this needed also for the NO3 channel? How is the temperature measured in channel 2?

The text is now clearer and additional information has been added. The relevant part now reads

"The first inlet, inlet 1, is used for sampling ambient air while the second inlet, inlet 2, is used to draw ambient air through a sheath encompassing channel 2 (see table 1), which measures ambient NO_3 concentrations. The sheath flow maintains the temperature of channel 2 (the temperatures of the cavities are measured using PT1000 temperature sensors equally spaced along the cavity tubes) at ambient temperature. This minimises the potential for perturbation of the N_2O_5/NO_3 equilibrium due to heating of the sample as it enters the aircraft cabin."

166: Is there a reason the flow is provided as a volume flow?

The volumetric flow is used to maintain a constant residence time. This is now mentioned in the text.

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171: This should be worded differently, as a modelling study cannot prove the statement. Could one not measure the efficiency?

The text is now clearer and takes into account the comments of reviewer #1. The relevant part now reads:

"A modelling study simulating the flow conditions (i.e. flow rates, flow line geometries etc.) gave dissociation efficiencies of N_2O_5 greater than 99.6% for a range of inlet air temperatures (-20 to 20 °C) and NO_2 concentrations (2 to 60 ppb). The expectation is that the efficiency is therefore sufficiently close to unity c.f. other sources of error (as is detailed in Sect.3) that 100% conversion efficiency is assumed."

279: mention Crowley's coefficient here

Text now reads

"The first order uptake coefficient of NO_3 to PFA, shown in Fig. 5, was found to be 0.27 s^{-1} ± 0.02 s^{-1}, which is in good agreement with that measured by Crowley et al. (2010) (0.25 s^{-1})."

290: Since the inlet outside the aircraft is probably not produced from PFA, shouldn't its effect be mentioned here as well?
The inlet outside the aircraft contains a PFA insert. All wetted parts in the instrument are made from PFA.

301: Only an upper limit for the KNO3 wall loss is known; wouldn't this affect the calculations using R2-R4?
It implies that $k_{N2O5loss}$ is also an upper limit, which is now mentioned in the text (note that direct wall losses of N2O5 are negligible even when using the upper limit of $k_{N2O5loss}$).

385: What is the pressure inside the cavities for these measurements? Which absolute humidity values were used for the measurement?
This information has been added to the text, which now reads:
"In both channels 1 and 2, the length of the detection cell occupied by the sample is 85% of the distance separating the cavity mirrors. This was determined by comparison of ground based water vapour measurements in both cavities (under standard conditions and with the mirror sheath flow) to those reported by a commercial hygrometer (the measured absolute humidity was 1.4%)."

391: The N2 flow could also extend into the cavity which would be no slow diffusion process. How would that affect your error calculation?
See answer to previous comment.

482 Detection limits should be provided with the corresponding pressure level (or cite detectable molecular density).
Detection limits are now quoted, in each case, with the corresponding pressures.

484 Shorter averaging time does not change sensitivity (if statistical noise prevails). What it does change is the minimum detectable concentration.
Sensitivity has now been changed to detection limits or detection performance where appropriate.

500 These values should be quoted as 2,4 and 1,0 pptv
Done

516 Is SeptEx also a campaign name?
This is now clearer in the text, which reads
"The flights during August 2010 and September 2010 were associated with a measurements campaign, SeptEx, and included seven daytime flights and a dawn and a dusk flight."

527 and 528: These values should be quoted as 548 +/- 3 and 80,0 +/- 1,0 ppt
Done

530 Ditto, 21,0 +/- 2,6 %
Done

522-531: Is there a reason for the three different integration times?
This is related to the sensitivity of each channel. The following sentence has been added at the end of the paragraph:
"Note that the integration time used for each of the three channels was chosen to achieve the desired detection performance (see discussion on signal integration time and detection limits in Sect 4.1)."

532 How good is the extraction of the pressure from this absorption feature?
The following sentence has been included in the text for clarification:
Monitoring the absorption of O_4 carries information about the pressure inside channel 3 during flight (which, in general, is of the order of that reported by instrument's pressure sensors, which were introduced in Sect.

2.2) and, at ground level, provides an independent verification of mirror reflectivity determination (Langridge et al., 2006).

534, 569, 596: Future publication announcements should be eliminated from the paper's main text; they can be mentioned in the outlook.
Done

606: If I understood correctly, the method (phase shift CRD) was already developed and is just implemented here with a (in my opinion) minor change: the use of a 5nm FWHM filter instead of a monochromator. This is not a refined version but instead a simpler measurement of only the peak mirror reflectivity and should be worded accordingly.
We think it a superior method for performing reflectivity measurements in difficult environments and therefore consider it to be refined.

630: Please spell out MD and NERC. Bill Dube and Steve Brown should be cited with
their respective institutes.
Done

Fig. 3: In general, tubing and flow lines should be bigger. In the middle, the text "Flow controllers" points to the wrong parts. The flow meters should be bigger and the middle ones seem to point in the wrong direction. The connection between the cross after the first valve after the N2 bottle is not clear to me.
Figure updated as suggested

Fig. 7: The decision in the diagram should be drawn as a diamond. No and Yes should be used to mark the different ways (not in a rectangle).
Figure updated as suggested
Fig. 8: Lines must be bigger
Figure updated as suggested
826 (gradients of)
Done
833: 1 s integration time(s)
Done
836: The values should be cited as 2,4 and 1,0 ppt
Done
Fig. 10, 3rd picture: Value should be cited as 548,0 +/- 3,0 ppt
Done
4th picture: 80,0 +/- 1,0
Done
6th picture: 21,0 +/- 2,6 %
Done
Fig. 13: Since the NO2 concentration values of interest are between 0 and _1000
pptv, the figure axis should be chosen accordingly (or a zoom should be added).
Axes changed
175 than (that)
Done
176 enters (into) channel 1
Done
176 ID and OD should be defined at least once
Defined at first use
241 (at)
Done
252 section 3.1.3 (3.2.3)
Done
308 is (was)
Done

346 the determination
Done
351 to the retrieved
Done
365 and in the
Done
368 Hitran 2008 database
Done
396 (,)
Done
13 inaccuracy
Done
18 often (usually)
Done
430 higher (more)
Done
506 limit(s)
Done
514 were conducted
Done
538 took (-) off
Done
518 airport(s)
Done
520 from continental (near) Europe
Done
524 (from of the)
Done
440 for longer times
Done
461 Allan (Allen) - this is wrong in a few instances throughout the paper
Done
483 worse (less) than the (that) values quoted
Done

References

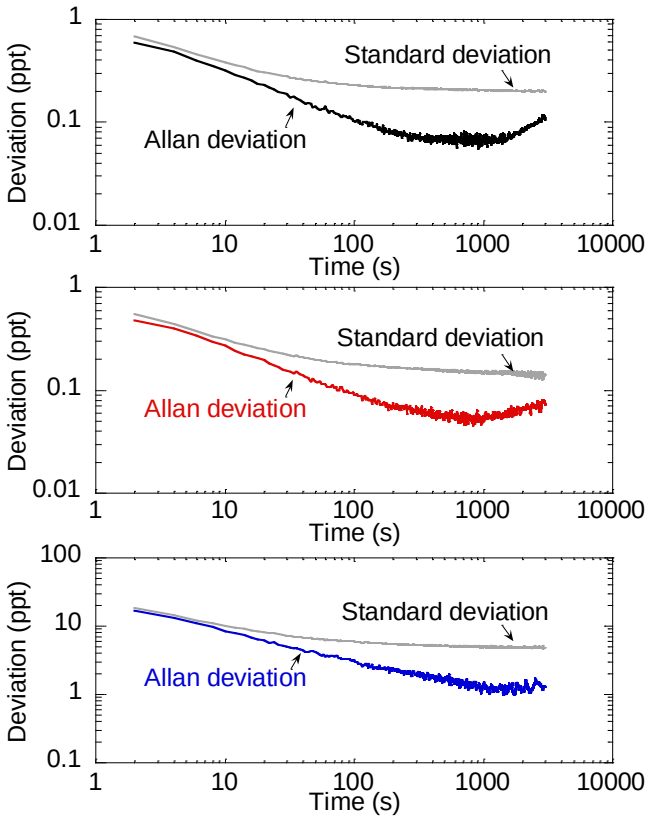
Ball, S. M., Langridge, J. M., and Jones, R. L.: Broadband cavity enhanced absorption spectroscopy using light emitting diodes, Chemical Physics Letters, 398, 68-74, 10.1016/j.cplett.2004.08.144, 2004.

Langridge, J. M., Ball, S. M., Shillings, A. J. L., and Jones, R. L.: A broadband absorption spectrometer using light emitting diodes for ultrasensitive, in situ trace gas detection, Review of Scientific Instruments, 79, 123110

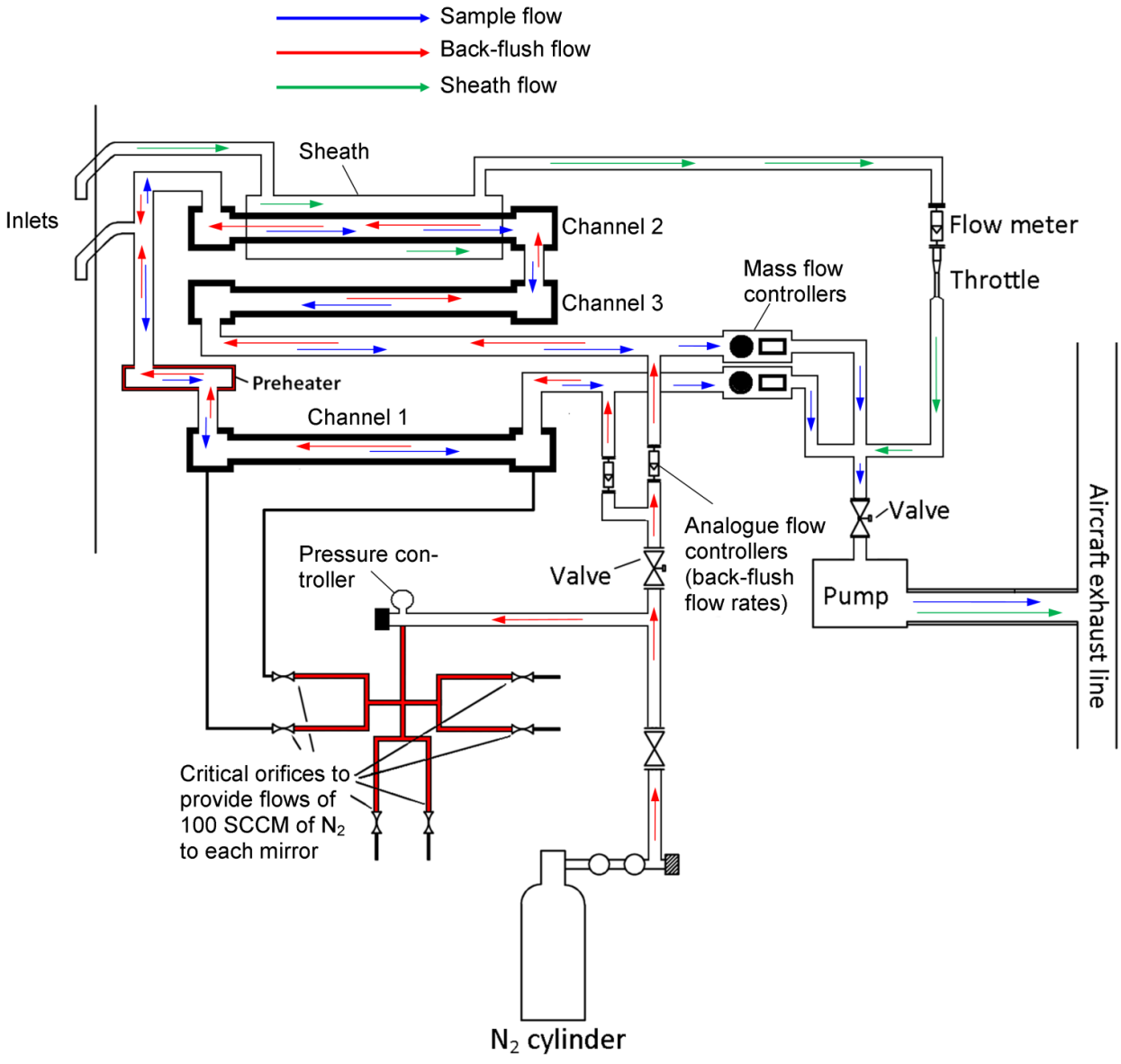
10.1063/1.3046282, 2008.

Thalman, R., and Volkamer, R.: Inherent calibration of a blue LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode, Atmos. Meas. Tech., 3, 1797-1814, 10.5194/amt-3-1797-2010, 2010.

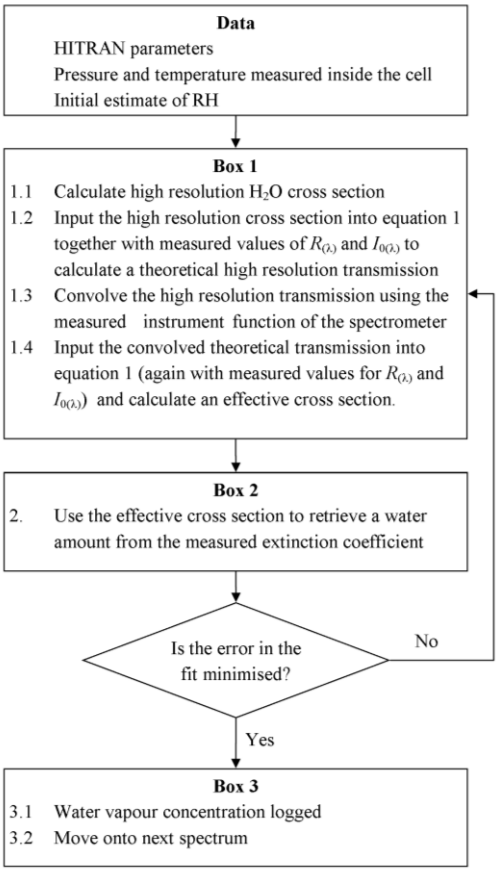
Varma, R. M., Venables, D. S., Ruth, A. A., Heitmann, U., Schlosser, E., and Dixneuf, S.: Long optical cavities for open-path monitoring of atmospheric trace gases and aerosol extinction, Appl. Opt., 48, B159-B171, 2009.


Deviation (ppt)
Time (s)
Standard deviation
Allan deviation
1
0.1
0.01
100
10
1
0.1
1
10
100
1000
10000

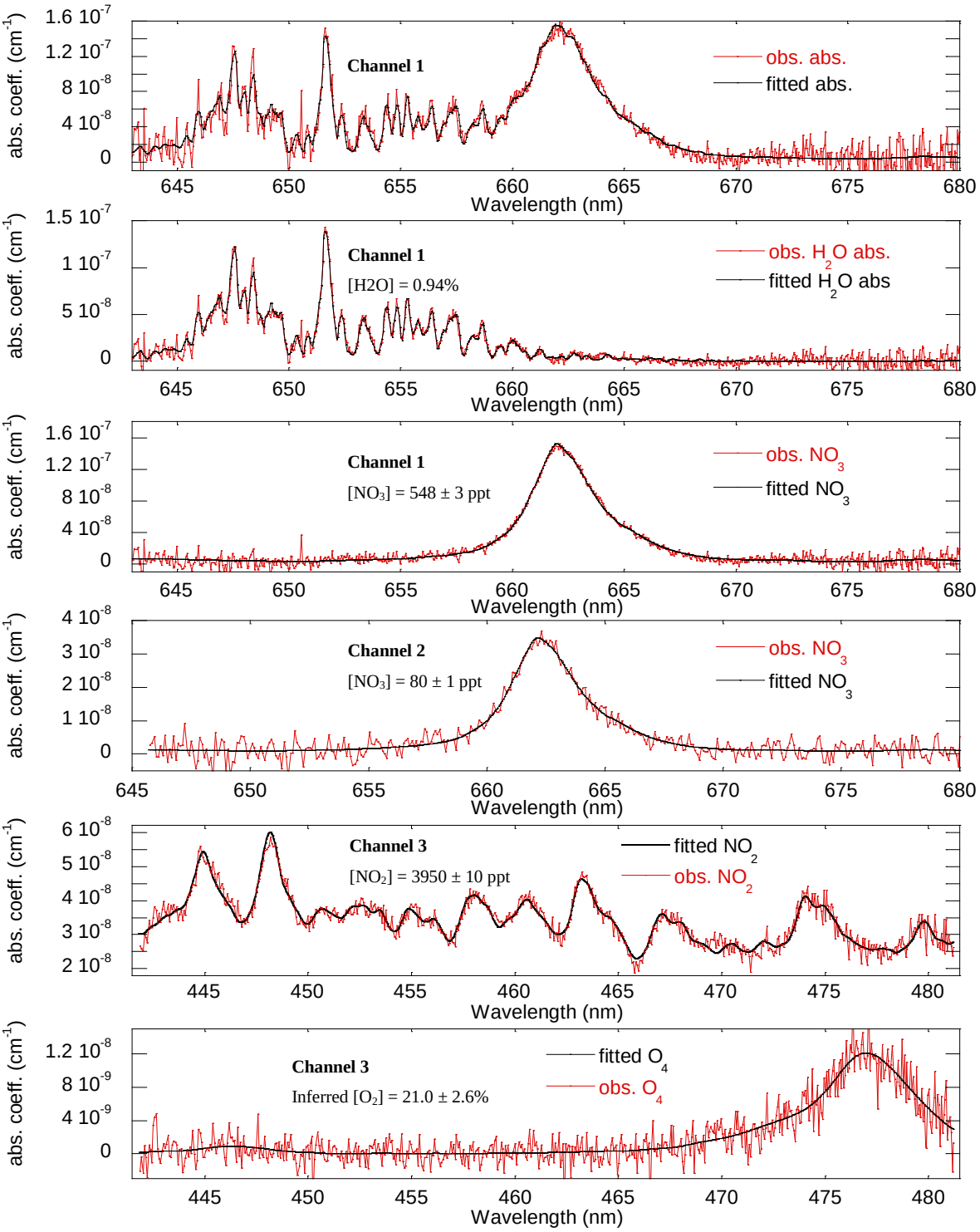
309

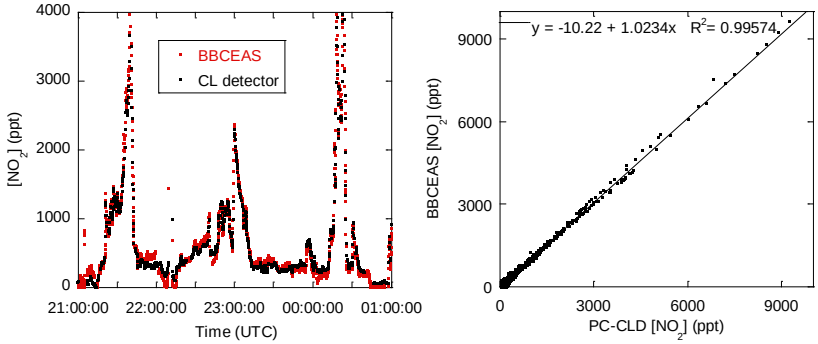

Sample flow
Back-flush flow
Sheath flow
Inlets
Sheath
Channel 2
Channel 3
Channel 1
Preheater
Flow meter
Throttle
Mass flow controllers
Valve
Analogue flow controllers (back-flush flow rates)
Pressure con-troller
Valve
Pump
Aircraft exhaust line
Critical orifices to provide flows of 100 SCCM of N_2 to each mirror
N_2 cylinder

310


Data
HITRAN parameters
Pressure and temperature measured inside the cell
Initial estimate of RH
Box 1
1.1 Calculate high resolution H_2O cross section
1.2 Input the high resolution cross section into equation 1 together with measured values of $R_{(\lambda)}$ and $I_{0(\lambda)}$ to calculate a theoretical high resolution transmission
1.3 Convolve the high resolution transmission using the measured instrument function of the spectrometer
1.4 Input the convolved theoretical transmission into equation 1 (again with measured values for $R_{(\lambda)}$ and $I_{0(\lambda)}$) and calculate an effective cross section.
Box 2
2. Use the effective cross section to retrieve a water amount from the measured extinction coefficient
Is the error in the fit minimised?
No
Yes
Box 3
3.1 Water vapour concentration logged
3.2 Move onto next spectrum

311


Channel 1
obs. abs.
fitted abs.
abs. coeff. (cm-1)
Wavelength (nm)
Channel 1
[H2O] = 0.94%
obs. H2O abs.
fitted H2O abs
Channel 1
[NO3] = 548 ± 3 ppt
obs. NO3
fitted NO3
Channel 2
[NO3] = 80 ± 1 ppt
obs. NO3
fitted NO3
Channel 3
[NO2] = 3950 ± 10 ppt
fitted NO2
obs. NO2
Channel 3
Inferred [O2] = 21.0 ± 2.6%
fitted O4
obs. O4


BBCEAS
CL detector
[NO2] (ppt)
Time (UTC)
y = -10.22 + 1.0234x R2= 0.99574
BBCEAS [NO2] (ppt)
PC-CLD [NO2] (ppt)