Title	A new cavity ring-down instrument for airborne monitoring of N2O5, NO3, NO2 and O3 in the upper troposphere lower stratosphere
Authors	Goulette, Marc;Brown, Steven S.;Dinesan, Hemanth;Dubé, W. P.;Hübler, Gerhard;Orphal, Johannes;Ruth, Albert A.;Zahn, Andreas
Publication date	2016-07
Original Citation	Goulette, M., Brown, S., Dinesan, H., Dubbé, W., Hübler, G., Orphal, J., Ruth, A. and Zahn, A. (2016) 'A New Cavity Ring-down Instrument for Airborne Monitoring of N2O5, NO3, NO2 and O3 in the Upper Troposphere Lower Stratosphere'. OSA technical Digest (online). Imaging and Applied Optics 25–28 July 2016, Heidelberg. Optical Society of America, LTh1G.2. doi:10.1364/LACSEA.2016.LTh1G.2
Type of publication	Conference item
Link to publisher's version	10.1364/LACSEA.2016.LTh1G.2
Rights	© 2016 The Authors; OSA 2016
Download date	2024-09-11 16:38:09
Item downloaded from	https://hdl.handle.net/10468/3481

A new cavity ring-down instrument for airborne monitoring of N_2O_5, NO_3, NO_2 and O_3 in the upper troposphere lower stratosphere

Marc Goulette (1), Steven S. Brown (2), Hemanth Dinesan (1), William P. Dubé (2), Gerhard Hübler (2), Johannes Orphal (3), Albert A. Ruth (1), and Andreas Zahn (3)

(1) Physics Department and Environmental Research Institute, University College Cork, Cork, Ireland, (2) NOAA Earth System Research Laboratory, R/CSD7, 325 Broadway, Boulder, CO 80305, USA, (3) Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, D-76344 Eggenstein-Leopoldshafen, Germany

Author e-mail address: marc.goulette@ucc.ie

Abstract: A new airborne instrument based on pulsed cavity ring-down spectroscopy for simultaneous detection of N_2O_5, NO_3, NO_2 and O_3 in the upper troposphere lower stratosphere is being developed for global atmospheric monitoring.

OCIS codes: 010.0010, 120.0120, 140.0140, 280.0280, 300.0300, 300.6260, 300.6360.

1. Introduction

The nitrate radical, NO_3 and its reservoir species, dinitrogen pentoxide (N_2O_5) are important trace gases in the regulation of both tropospheric and stratospheric ozone [1]. NO_3 is formed by reaction of ozone with NO_2, and reacts with NO_2 to reversibly form N_2O_5 :

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1}$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \tag{2}$$

In situ detection of NO_3 and N_2O_5 in the upper troposphere lower stratosphere (UTLS) represents a new scientific direction as the only previous measurements of these species in this region of the atmosphere has been via remote sensing techniques. Because these species are potentially stratified spatially, their mixing ratios, and their influence on nitrogen oxide and ozone transport and loss at night can show large variability as a function of the altitude. Aircraft-based measurements of heterogeneous N_2O_5 uptake in the lower atmosphere have uncovered a surprising degree of variability in the uptake coefficient [2], but there are no corresponding measurements at high altitude.

The UTLS is routinely sampled by the IAGOS-CARIBIC program (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, www.caribic-atmospheric.com), a large scale European infrastructural program with the aim of studying global climate change, in particular the chemistry and transport across this part of the atmosphere [3]. A container (Fig. 1) with 15 different automated instruments from 8 European research partners is currently flying on board a commercial Lufthansa aircraft A340-600 since 2005 to monitor about 100 atmospheric species (trace gases and aerosol parameters) in the ULTS. CARIBIC has already completed more than 434 flights across the globe (Fig. 2).

Fig. 1. CARIBIC container (1.6 tons), 15 instruments in 9 racks, ~ 100 trace gas species and aerosol parameters, 13 European institutions (6 countries), 1-2 flights per month.

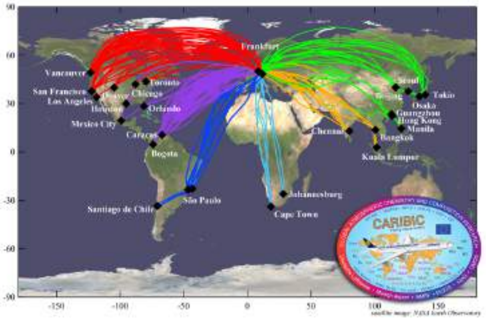

Fig. 2. CARIBIC flight routes from May 2005 to February 2016 (434 flights).

2. Description of the instrument

Cavity ring-down spectroscopy (CRDS) is a high sensitivity, direct absorption technique based on the measurement of the time constant for single exponential decay of light intensity leaking from a stable optical cavity [4]. Measurement of this time constant in the presence (τ) and absence (τ_0) of an absorbing species gives an absolute measurement of the absorption coefficient, α [cm^{-1}], and, therefore, the absorber's mixing ratio, (A) [$molecules.cm^{-3}$] as long as the absorption cross section, σ [$cm^2.molecule^{-1}$] and the transmission efficiency for the target compound through the inlet system, T_E, are known:

$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \tag{3}$$

$$(A) = \alpha \frac{R_L}{\sigma \cdot T_E} \tag{4}$$

Here c is the speed of light, and R_L is the ratio of the cavity length to the length over which the sample is present in the cavity.

During the past decade, a large number of instruments based on cavity ring-down spectroscopy have been built and tested in different environment (both in the field and on aircrafts). The new instrument (Fig. 3) will be similar to the devices successfully deployed on NOAA aircrafts, such as ARNOLD or NOxCaRD [5-7]. The overall size, weight, and power consumption of the instrument are 590 x 500 x 448 cm^3, 60 kg, and 320 W, respectively. The air sampled underneath the cargo bay of the aircraft is distributed inside the instrument through a dedicated inlet system (Fig 4) distributing the flow to the cavities, as described below.

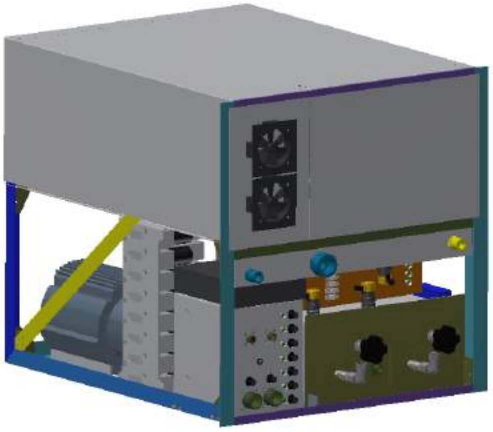

Fig. 3. Schematic of the new instrument.

Fig. 4. Dedicated inlet system of the Airbus A340-600.

Figure 5 shows the layout of the optical and data acquisition systems for the instrument. The detection is based on 4 high-finesse optical cavities (cavity length ~ 44.1 cm, expected finesse ~ 627 000, expected path length ~ 176 km, τ_0 ~ 30 µs). Two cavities are operated at 662 nm (maximum absorption of NO_3), the other two at 405 nm (maximum absorption of NO_2). The inlet to one of the (662)-cavities is heated in order to thermally decompose N_2O_5 entirely to provide the sum of NO_3 and N_2O_5, with N_2O_5 provided by the difference to a direct NO_3 measurement in a separate, unheated channel. One of the (405)-cavities is flushed continuously with NO in order to measure O_3 concentrations via quantitative conversion to NO_2.

Each cavity is set up near the confocal geometry. The mirrors have a 1" diameter, 0.5 m radius of curvature, and a nominal reflectivity of R=99.9995% at 662 nm and R=99.9993% at 405 nm. Dry air is continuously flushed to purge the mirrors during measurement, to maintain mirror cleanliness. The light coming out of the cavities is detected by 4 photomultiplier tubes (PMTs), and sent to the data acquisition (DAQ) system. The digitization, analysis, and the fitting of the exponential decays will all be implemented in the Labview software. The instrument has been designed to operate continuously for a duration of 50 hours (4 flights) with a time resolution of 1s. A gas flow system consisting of a pump, mass flow controllers, pressure gauges, electronic valves, and temperature controllers is used to minimize species losses and concentration fluctuations and to optimize the duty cycle and time resolution. To maintain a constant residence time within the flow systems, the DAQ software sets the different flow rates to a constant volumetric flow as the cell pressure changes with aircraft altitude. The flow rates will be around 2 slpm (standard litre per minute) for the NO_2 and O_3 cavities, and about 6-8 slpm for the NO_3 and N_2O_5 cavities. To remove particles that can significantly contribute to the extinction measured in the cavity, the sampled air passes through a Teflon filter (PTFE, 2-μm pore size, 25 μm thick) upstream of the cavities.

All the structural parts (such as front plates), as well as the frame of the instrument, are made of Aluminium 7075. All other brackets or sheet metals are made of Aluminium 2024. An EMI/RFI electrical box has been installed to minimize the electromagnetic and radio frequency interferences. Therefore many aspects will have to be studied for the construction of the instrument.

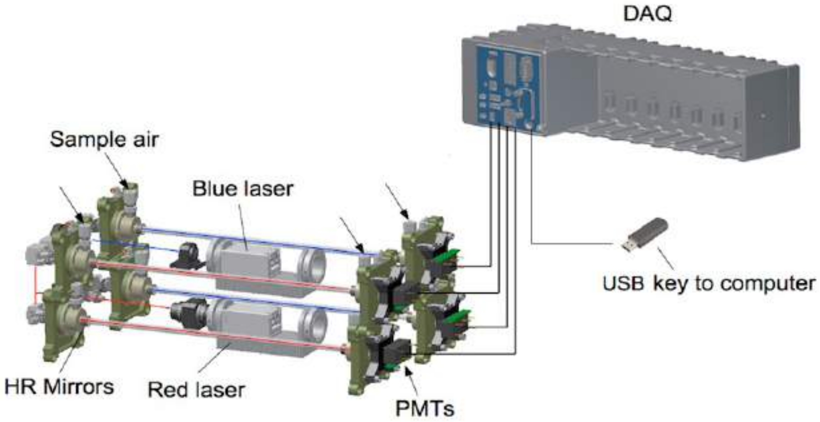

Fig. 5. Layout of the optical and data acquisition systems.

3. Discussion and future work

The design of the instrument has been completed at the end of 2015, the construction is currently on-going, and the device will be tested in the lab during summer 2016. If successfully executed, the instrument is expected to be installed in the CARIBIC container during winter 2016-2017.

A preliminary estimate of the expected detection limits in the field yielded approximately 0.8 pptv (1 s) for NO_3, 1.0 pptv (1 s) for N_2O_5, 25 pptv (1 s) for NO_2, and 5 pptv (1 min) for O_3. The main limitations include inlet transmission efficiencies, ring-down time accuracy, temperature dependence of the cross-sections, sampling rate of the DAQ system, and flow-related noise in the cavities, especially for the heated channel [5-8]. The instrument is expected to deliver data between 2017 and 2020.

4. References

[1] S.S. Brown, J. Stutz, "Nighttime radical observations and chemistry", Chem. Soc. Rev., 41, (2012) 6405-6447.

[2] S.S. Brown, T.B. Ryerson, A.G. Wollny, C.A. Brock, R. Peltier, A.P. Sullivan, R.J. Weber, J.S. Holloway, W.P. Dubé, M. Trainer, J.F. Meagher, F.C. Fehsenfeld, A. R. Ravishankara, "Variability in nocturnal nitrogen oxide processing and its role in regional air quality", Science, 311 (2006) 67-70.

[3] C.A.M. Brenninkmeijer et al., "Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system", Atmos. Chem. Phys. 7 (2007) 4953-4976.

[4] M.D. Wheeler, S.M. Newman, A.J. Orr-Ewing, M.N.R. Ashfold, "Cavity ring-down spectroscopy", J. Chem. Soc., Faraday Trans., 94 (1998) 337-351.

[5] W.P. Dubé, S.S. Brown, H.D. Osthoff, M.R. Nunley, S.J. Ciciora, M.W. Paris, R.J. McLaughin, A.R. Ravinshanka, "Aircraft instrument for simultaneous, in situ measurement of NO3 and N2O5 via pulsed cavity ring-down spectroscopy", Rev. Sci. Instrum., 77 (2006) 034101.

[6] N.L. Wagner,, W.P. Dubé, R.A. Washenfelder, C.J. Young, I.B. Pollack, T.B. Ryerson, S.S. Brown, "Diode laser-based cavity ring-down instrument for NO3, N2O5, NO, NO2 and O3 from aircraft", Atmos. Meas. Tech., 4 (2011) 1227-1240.

[7] H. Fuchs, W.P. Dubé, B.M. Lerner, N.L. Wagner, E.J. Williams, and S.S. Brown, "A sensitive and versatile detector for atmospheric NO2 and NOx based on blue diode laser cavity ring-down spectroscopy", Environ. Sci. Technol., 43 (2009) 7831-7836.

[8] H. Fuchs, W.P. Dubé, S.J. Ciciora, S.S. Brown, "Determination of Inlet Transmission and Conversion Efficiencies for in Situ Measurements of the Nocturnal Nitrogen Oxides, NO3, N2O5 and NO2, via Pulsed Cavity Ring-Down Spectroscopy", Anal. Chem., 80 (2008) 6010-6017.