Atmos. Meas. Tech. Discuss., 7, 11593–11652, 2014 www.atmos-meas-tech-discuss.net/7/11593/2014/ doi:10.5194/amtd-7-11593-2014 © Author(s) 2014. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

Retrieval and validation of carbon dioxide, methane and water vapor for the Canary Islands IR-laser occultation experiment

V. Proschek¹, G. Kirchengast¹, S. Schweitzer^{2,1}, J. S. A. Brooke³, P. F. Bernath^{4,3}, C. B. Thomas³, J.-G. Wang³, K. A. Tereszchuk^{5,3}, G. González Abad^{6,3}, R. J. Hargreaves^{4,3}, C. A. Beale^{4,3}, J. J. Harrison³, P. A. Martin⁷, V. L. Kasyutich^{8,7}, C. Gerbig⁹, O. Kolle⁹, and A. Loescher¹⁰

 ¹Wegener Center for Climate and Global Change (WEGC) and Institute for Geophysics, Astrophysics and Meteorology/Institute of Physics (IGAM/IP), University of Graz, Graz, Austria
 ²Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesm.b.H., Weiz, Austria
 ³Department of Chemistry, University of York, York, UK
 ⁴Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia, USA
 ⁵Environment Canada, Toronto, Ontario, Canada
 ⁶Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA
 ⁷School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, UK
 ⁸Servomex, Jarvis Brook, Crowborough, UK



⁹Biogeochemical Systems Department, Max-Planck-Institute for Biogeochemistry, Jena, Germany

¹⁰Earth Observation Future Missions Division, ESA/ESTEC, Noordwijk, the Netherlands

Received: 19 May 2014 - Accepted: 24 October 2014 - Published: 21 November 2014

Correspondence to: V. Proschek (veronika.proschek@uni-graz.at)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Discussion Paper		ITD 11652, 2014	
per Discussion Paper	valida greenhou for the Islands e	Retrieval and validation of greenhouse gases for the Canary Islands experiment V. Proschek et al.	
Daper			
Discussion Paper	Abstract Conclusions Tables	Introduction References Figures	
_	I∢ ∢	►I ►	
Discussion Pape	Full Screen / Esc Printer-friendly Version Interactive Discussion		
Discussion Paper	Back Full Scr Printer-frie	ndly Version	



Abstract

The first ground-based experiment to prove the concept of a novel space-based observation technique for microwave and infrared-laser occultation between Low Earth Orbit satellites (LMIO) was performed in the Canary Islands between La Palma and

- ⁵ Tenerife in July 2011. This experiment aimed to demonstrate the infrared-laser differential transmission principle for the measurement of greenhouse gases (GHGs) in the free atmosphere. Such global and long-term stable measurements of GHGs, accompanied also by measurements of thermodynamic parameters and line-of-sight wind in a self-calibrating way, have become very important for climate change monitoring.
- ¹⁰ The experiment delivered promising initial data for demonstrating the new observation concept by retrieving volume mixing ratios of GHGs along a ~ 144 km signal path at altitudes of ~ 2.4 km. Here, we present a detailed analysis of the measurements, following a recent publication that introduced the experiment's technical setup and first results for an example retrieval of CO₂. We present the observational and validation
- datasets, the latter simultaneously measured at the transmitter and receiver sites, the measurement data handling, and the differential transmission retrieval procedure. We also determine the individual and combined uncertainties influencing the results and present the retrieval results for ¹²CO₂, ¹³CO₂, C¹⁸OO, H₂O and CH₄. The new method is found to have a reliable basis for monitoring of greenhouse gases such as CO₂, CH₄, and H₂O in the free atmosphere.

1 Introduction

25

Several in situ and remote sensing measurement principles have already been applied for long-term greenhouse gas (GHG) monitoring from ground-based stations, airplanes, and even satellites. The most widely known, long-term, in situ, ground-based CO_2 measurements have been made at the Mauna Loa Observatory (Keeling, 1970). Measurements have been ongoing for some decades now, recording the





anthropogenically-induced increases in atmospheric CO₂ levels (From and Keeling, 1986; Heimann, 2005). Numerous complementary ground-based (Yang et al., 2002; Brailsford et al., 2012; Messerschmidt et al., 2012) or airborne (Desjardins et al., 1989; Gurk et al., 2008; Vadrevu and Choi, 2011) CO₂ measurement campaigns have been ⁵ conducted for validation and calibration purposes, e.g., the Total Carbon Column Observing Network (TCCON; Wunch et al., 2010).

Instruments on satellites, e.g., IASI (Infrared Atmospheric Sounding Interferometer; Chalon et al., 2001) on MetOp, AIRS (Atmospheric InfraRed Sounder; Chahine et al., 2006) on Aqua or SCIAMACHY (SCanning Imaging Absorption spectroMeter for

- Atmospheric CHartographY; Bovensmann et al., 1999) on Envisat and missions like GOSAT (Greenhouse gas Observing SATellite; Hamazaki et al., 2004; Yokota et al., 2009; Yoshida et al., 2011) measure GHGs remotely from space on a long-term basis, though with significant limitations in altitude resolution, geographic coverage and accuracy due to the use of passive radiometry techniques that are challenging to calibrate.
- ¹⁵ Very precise and accurate measurements of GHG concentrations and atmospheric parameters, including line-of-sight wind in the free atmosphere, self-calibrating and independent from external parameters, are needed for climate change observations. In order to serve as climate benchmark measurements, these observations need to be made over long time periods in very stable and concise ways meeting high qual-
- ity standards. The new Low Earth Orbit (LEO) satellite observation concept LEO-LEO Microwave and Infrared-laser Occultation (LMIO), introduced by Kirchengast and Schweitzer (2011), provides such a measurement technique.

This active remote sensing method uses the differential transmission principle (Kursinski et al., 2002; Gorbunov and Kirchengast, 2007; Kirchengast et al., 2010;

Kirchengast and Schweitzer, 2011; Schweitzer et al., 2011a) for accurately measuring GHG concentrations. In particular, each GHG is retrieved by the use of two closely spaced frequencies within the 2.0 to 2.5 µm spectral range "between" the solar and terrestrial emission spectra. The broadband effects of the atmosphere such as Rayleigh and aerosol scattering, scintillation, and even sub-visible cirrus cloud absorption are



removed by subtracting a nearby reference infrared-laser signal outside the GHG absorption lines ("off-signal") from an absorption signal located on a targeted GHG absorption line ("on-signal"). In several studies, including Kirchengast et al. (2010); Schweitzer (2010); Schweitzer et al. (2011a, b); Proschek et al. (2011, 2014), detailed insight is given into the mission concept, the scientific objectives, the retrieval process, and examples of retrievals that were performed.

The first proof of concept experiment, described by Brooke et al. (2012) and giving a technical overview of the ground-based experiment with preliminary results on CO_2 , was performed between La Palma and Tenerife in the Canary Islands in July 2011 (see Fig. 1). These sites enabled the realization of a long-path ground link (~ 144 km),

(see Fig. 1). These sites enabled the realization of a long-path ground link (~ 144 km), with both transmitter (Tx) and receiver (Rx) locations at an altitude of ~ 2.4 km. The Tx platform at La Palma, was mounted in the parking lot next to the Nordic Optical Telescope (NOT), and pointed towards the Rx telescope located at the Optical Ground Station (OGS) from ESA in Tenerife. At the OGS, a telescope with an aperture of 1 m in diameter was used to capture the infrared-laser signals, which were afterwards guided to a Rx breadboard.

The main part of the transmitter breadboard consisted of four tunable single-mode Distributed Feedback (DFB) lasers emitting in the Short-Wave Infrared (SWIR) spectral range. Absorption lines of the main CO₂ isotopes (¹²CO₂, ¹³CO₂, C¹⁸OO) and

- $_{20}$ H₂O were covered by two lasers near 2.1 μm and the other two lasers covered CH₄ absorption in the spectral range near 2.3 μm . For the latter case, only one laser was used for the retrieval calculations in this study, since the other one was measuring at a reference-signal location somewhat away from suitable absorption lines. Both spectral windows used within 2.0 to 2.4 μm are generally insensitive to H₂O saturation and
- the signals were sufficiently strong for long-path absorption by the targeted GHGs, even with relatively low-power lasers (between 4 and 10 mW).

From the Tx side, infrared spectral scans over periods of up to about 20 min, with 4 s sub-periods and spectral ranges of up to 2 nm from each of the IR-lasers, were transmitted into the atmosphere. The infrared signals experienced molecular absorption





and further broad-band atmospheric effects, such as scintillation, aerosol and Rayleigh scattering. The propagation beam path, for brevity termed ray path hereafter in this paper, was at all times running in the free atmosphere above the marine boundary layer, so that no low liquid clouds obscured the signals.

- ⁵ On the Rx side, the infrared-laser signals were captured by the OGS telescope. The signals were directed along the optical path of 39 m focal length into the Coudé room of the OGS, where they were focused onto the InGaAs photodiode detectors of the Rx breadboard assembly. A more detailed description of the setup and recording process is given by Brooke et al. (2012).
- In addition to the infrared spectra measured at the Rx, datasets for validation were recorded. The validation measurement instruments were located close to the Tx and Rx sites as listed in Table 1, where the (GPS-derived) positions of all measurement instruments used during the campaign are listed in terms of their latitude/longitude/altitude. Together, the IR-laser spectra and the validation data from these locations provided the basis for the detailed GHG retrieval analysis and measurement performance assess-

ment for CO_2 , CH_4 , and H_2O in this study.

The study is organized as follows. Based on the observed datasets summarized in Sect. 2 and on the related data processing and GHG retrieval described in Sect. 3, a detailed uncertainty analysis is conducted (Sect. 4) and finally the GHG retrieval results are discussed (Sect. 5). Summary and conclusions are given in Sect. 6.

2 Observational and validation datasets

2.1 Observational dataset

20

In the course of the field campaign, we effectively recorded useful datasets of infraredlaser transmission spectra during two nights, the 21 July and the 22 July 2011. We applied a "fast scan" mode (400 Hz native scan rate) for narrow ($\sim 1 \text{ cm}^{-1}$) or broadband (~ 3 to 4 cm⁻¹) spectral ranges. The raw data consist of alternative records of the



two active lasers (L1+L2 or L3+L4), which were alternatively activated for 4s at any one time within the whole measurement period (of up to \sim 20 min). The spectral ranges covered by the two active lasers typically were different, but also overlapped in some cases as some lasers were able to scan the same spectral regions. In a pre-processing, these raw data were averaged over 4s. A detailed description of the scanning/recording

process is given by Brooke et al. (2012), Sect. 2 and Appendix A therein.

10

The recorded set of measurements, summarized in Table 2, were deemed suitable for data retrieval as they contained adequate absorption lines, a sufficient spectral range, and an acceptable signal-to-noise ratio. This set contains 19 data files, measured in the two nights of the 21 and the 22 July. At bottom of the table, the two CH_4

- spectral range measurements are listed which were recorded at the end of the campaign during the night of 22 July. As can be seen from the third column of Table 2, three lasers (L1, L2, L3) effectively yielded useful absorption spectra; laser L4 covered no adequate CH_4 absorption lines (see also the discussion below in Sect. 3).
- ¹⁵ The number of spectra quoted in the fourth column of Table 2 denotes the number of 4 s-averaged spectra in a file, and thus gives the number of possible single retrieval results within the respective time period. Since different data files contain different wavenumber ranges, narrow or broadband, the starting (v_{start}) and ending (v_{end}) wavenumbers and associated range widths (Δv) are given as well. Furthermore, the duration of each of the recorded measurements is shown in the last three columns of
- ²⁰ duration of each of the recorded measurements is shown in the last three columns of Table 2. These columns represent the start time of the first 4 s scan (t_{start}), the end 4 s scan (t_{end}) and the total time (Δt) for each laser in the associated file.

Since the spectra were pre-processed and underwent basic quality control (Brooke et al., 2012, Appendix A therein), the recording time per data file varied from approxi-

²⁵ mately ~ 1 min up to nearly 30 min, depending on the stability of the conditions during the measurements. Hence, the files contain from just three up to more than 90 successfully processed 4s spectra. Putting the signal-to-noise ratio (SNR) achieved for this basic 4s averaging period of the experiment into context with the actual spaceborne LMIO method, the latter still achieves higher SNR with its 2 ms averaging period





during the fast vertical scan through the atmosphere, since its Tx-to-Rx link power budget is more favorable (Schweitzer et al., 2011a, ; Sect. 3.7 therein).

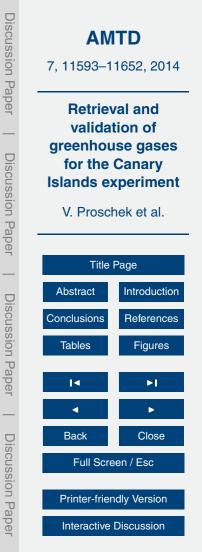
2.2 Validation dataset

A crucial complementary part of the measurement campaign was the recording of validation data to support the proof-of-concept of the GHG retrieval results from the longrange infrared-laser link. Two different measurement instrument sources on the Tx site and three on the Rx site enabled a validation of the GHG concentrations retrieved from the measured IR-laser data. Thereby it is important to take into account also limitations of the representativeness of these local measurements for the concentrations averaged over the IR-laser link. The data sources are listed in Table 3.

At the Tx site, we obtained meteorological data as a continuous 1 min-sampled dataset from the Nordic Optical Telescope (NOT) weather station, containing the pressure (p) in Pa, temperature (T) in K, relative humidity (RH) in percent, and the wind speed (V) in m s⁻¹. Additionally, a CRDS (Cavity Ring-Down Spectrometer, model G1301-m Picarro Inc. CA, USA) continuously recorded the CO. H O and CH, drive

- G1301-m, Picarro Inc., CA, USA) continuously recorded the CO₂, H₂O, and CH₄ dryair mole fraction in ppm, at a time resolution of 2.5 s. CRDS measurement accuracy was within the compatibility targets of 0.1 ppm (CO₂), 2 ppb (CH₄), and 5% (H₂O) (WMO, 2012). The CRDS was calibrated before and after the campaign against ambient air standards traceable to the respective WMO scales for CH₄ and CO₂, and
- ²⁰ against a NIST traceable dewpoint mirror for H₂O; no significant drift was observed. In this paper we refer to volume mixing ratio (\mathcal{V}) in ppmv, since this is the unit given for our retrieval results, rather than to mole fraction (the differences being not relevant for the limited accuracy needed here). The inlet of the CRDS was installed about 2 m above the roof of the NOT service building, aiming at locally undisturbed and clean air ²⁵ conditions.

At the Rx site, the same set of meteorological observables as at the Tx site was available from the weather station of the Global Oscillation Network Group (GONG), comprising p, T, RH and V again as 1 min-sampled data. A second CRDS instrument





installed at the Rx site recorded the same set of GHGs as at the Tx site, and with the same time resolution and accuracy. In this case, the inlet was mounted 2 m over the ground and about 4 m from the dome of the OGS, again aiming to ensure undisturbed and clean air conditions. In addition, we collected air sample flasks at the Rx site. The

inlet for these flasks was placed next to the CRDS inlet. The sample flasks were filled roughly every 3 h during the measurement times, and were analyzed 4 months after the campaign at the gas analytics and isotope laboratories of the Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, determining the isotope ratios δ¹³CO₂ and δC¹⁸OO as well as the dry-air mole fractions of CH₄ with an accuracy that lies well within the compatibility goals recommended by WMO (2012) of 0.01, 0.05 permil, and 2 ppb, respectively.

Additionally, auxiliary three-dimensional meteorological analysis field data from the European Centre for Medium-Range Weather Forecasts (ECMWF) were acquired over a 330 km × 330 km area comprising the Canary Islands, providing high-resolution six-

- ¹⁵ hourly analyses of the local pressure, temperature, and humidity conditions during the campaign period. These ECMWF analysis fields were used for (co-located) crosscheck of the local meteorological data from the weather stations at the Tx and Rx sites, for providing the meteorological information for realistic ray tracing along the Txto-Rx signal propagation path, and for providing the needed ray path-averaged mete-
- orological parameters for determining the GHG volume mixing ratios from differential transmissions during the iteration calculations of the retrieval process (see Sect. 3.2 for details).

In Fig. 2, the validation datasets are illustrated, spanning over the time of the measurement campaign during which useful transmission data were acquired. In particular,

the data over the 48 h from 12:00 UTC on the 20 July to 12:00 UTC on the 22 July are shown. The vertical dotted lines indicate the three infrared-laser measurement time windows within which all measurement files summarized in Table 2 were acquired.

In the top panel of Fig. 2, where temperature and pressure are illustrated, the gray-shadings indicate a +1% temperature deviation and a -1% pressure deviation,





respectively. These percentage deviations correspond to the deviations of the weather stations values from the co-located ECMWF values, which were found to occur in a rather stable manner from cross-checking the data during the times of infrared-laser link measurements at both the Tx and Rx locations. During the measurement times,

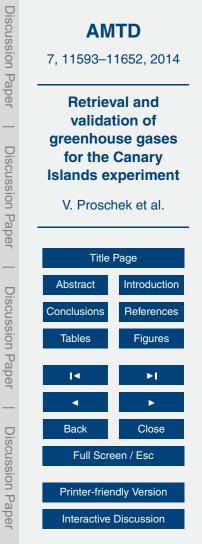
⁵ both temperature and pressure evidently undergo rather weak fluctuations of up to about 2 K and 2 hPa only, i.e., the thermodynamic conditions have been fairly stable during these nighttimes.

In the upper-middle panel, where the H₂O volume mixing ratio (\mathcal{V}_{H_2O}) is illustrated, the CRDS data are shown as measured (just 10 min-averaged) while the \mathcal{V}_{H_2O} from the weather stations was derived from the relative humidity, temperature, and pressure measurements by standard meteorological equations applicable in moist air. It is evident that a significant negative deviation of the meteorological station data to the CRDS data exists at the Tx site, while a significant positive deviation occurs at the Rx site. These longer-time-scale deviations seem to be systematic, while the smallertime-scale fluctuation patterns of the CRDS and the weather station data resemble each other fairly well.

Therefore, we interpret the deviations as primarily being a bias of the weather station data, since the CRDS measurements underwent calibrations before and after the campaign with negligible instrument drift. Possibly the humidity sensor of the weather station provides low accuracy, though no clarification could be found from local weather station operators. Thus, the CRDS data are considered more trustworthy. They are also in better overall agreement with the comparatively smooth ECMWF data, which show weak sensitivity regarding the local moisture variations. The reason is that the ECMWF grid resolution (about 14 km) and time resolution (6 h) are much coarser than the local

²⁵ variability so that local variations are strongly smoothed.

Inspecting the moisture conditions during the IR-laser link measurement times, the \mathcal{V}_{H_2O} data indicate a strong difference of up to about 0.8% between the Tx and Rx site. This significant horizontal variation from La Palma to Tenerife suggests assuming conservative bounds of representativity of the in situ values for the along-ray conditions.





We will therefore assume a rather high relative uncertainty (of ~ 50 %) for the knowledge of H_2O concentration from the validation data, as seen below in Sect. 4.

The lower-middle panel of Fig. 2 shows the CRDS data for CO_2 and CH_4 , which generally exhibit somewhat stronger variability at the Tx site, indicating more capacity

for local-scale meteorological and composition fluctuations at this site. Furthermore, an anti-correlated link between the CO₂ and CH₄ variations, and also a link to the H₂O variations (upper-middle panel), is clearly visible, i.e., CO₂ increases are associated with CH₄ decreases and H₂O increases. The magnitude of the variations is small, though, both over time and regarding the differences between the Tx and Rx sites, amounting to relative changes of only about 1 to 2% in these well-mixed GHG volume mixing ratios.

For completeness, the bottom panel shows the wind speeds at both the Tx and Rx sites. The wind speeds at the Tx site are systematically stronger by a factor of two to three. This is primarily due to the specific topographical conditions at the Tx

- site at La Palma around the NOT parking lot, where a rather steep outer hillslope on the one side meets with a steep wall down into the volcanic crater not far away on the other side. The surroundings of the OGS telescope at Tenerife at the Rx site are much smoother; this location is characterized by an extended gentle hillslope in the surroundings. The stronger dynamics at the Tx site is also reflected in the stronger
- ²⁰ GHG dynamics noticed in the panels above, in particular during the night. The Tx wind speeds were persistently above 10 m s⁻¹, and frequently of up to about 15 m s⁻¹, posed challenges to the stability of the Tx telescope pointing towards the OGS during the IR-laser link measurement sometimes, so that occasional re-adjustments were necessary (Brooke et al., 2012).
- In order to provide context information for water vapor, the most variable species along the Tx-to-Rx ray path, Fig. 3 visualizes the H₂O volume mixing ratio (\mathcal{V}_{H_2O}) variation along the ray path based on ECMWF analysis data. The \mathcal{V}_{H_2O} values vary considerably between about 0.1 and 0.5%, whereby the spread is smaller during the first measurement night than during the second night. The high horizontal variability





indicated here further underscores the necessity to assign a conservative uncertainty range to the water vapor knowledge available from the validation data.

3 Data processing setup and retrieval algorithm

3.1 Data processing setup

- In this section, we will explain the pre-investigations and preparation steps for the retrieval procedure. The key tool for our retrieval and for the preparatory work is the Reference Forward Model (RFM) from Dudhia (2008). This tool enables the calculation of line-by-line absorption spectra as well as forward simulations of single-line and individual-frequency transmissions and absorption coefficients for targeted GHGs.
- The RFM uses as a basis the HIgh resolution TRANsmission molecular absorption database 2008 (HITRAN08; Rothman et al., 2009), comprising spectroscopic parameters for every trace species absorption line, such as the transition frequencies of absorption line peaks, the line intensity, and air- and self-broadened halfwidths, plus estimated uncertainties of these parameters.
- As simple model for expected GHG concentrations, we invoked the Fast Atmospheric Signature Code model (FASCODE, 2008). More specifically, we adopted a basic set of volume mixing ratios *V* for four GHGs, namely 380 ppmv of CO₂, 1.7 ppmv of CH₄, 0.32 ppmv of N₂O, and 0.13 ppmv of CO, all assumed to be homogeneously mixed in the atmosphere, i.e., with no volume mixing ratio changes in the ray path domain.
 For H₂O, we used the variable concentrations from the ECMWF analysis fields and
- For H_2O , we used the variable concentrations from the ECMWF analysis fields pressure and temperature were as well taken from these fields.

3.1.1 Absorption and reference line allocation

The first important step was to find adequate absorption lines of GHGs in the available IR-laser scanned spectral regions for the following set of GHGs: $X = {{}^{12}CO_2, {}^{13}CO_2, }$





C¹⁸OO, CH₄ H₂O}. The last two are meant to be the main isotopes of methane and water vapor. All isotopes of a GHG make up a certain ratio of the total concentration of this GHG, with the isotopic abundance factors taken from HITRAN08. Given all the uncertainties involved in this basic IR-laser demonstration experiment (discussed further below), more recent factors or more refined mole fraction values are not needed.

- The set *X* of GHGs and the corresponding absorption line center frequencies, plus the chosen reference frequencies, are listed in Table 4. We selected ten usable absorption lines, including two for ${}^{12}CO_2$, one for ${}^{13}CO_2$, three for $C{}^{18}OO$, two for H₂O, and two for CH₄. In order to avoid broadband effects the reference frequencies are selected close by, as in the satellite-based IR-laser occultation concept, within a spectral distance of 0.15 to 0.35 cm⁻¹. The rightmost two columns of Table 4 additionally show the HITRAN08 uncertainty estimates of the two spectroscopic parameters found to be of primary relevance to the overall uncertainty in our context here, the line intensity uncertainty ΔS and the air-broadened halfwidth uncertainty $\Delta \gamma_{air}$. The impact of these
- ¹⁵ two (considerable) uncertainties will be discussed later in Sect. 4.

In Fig. 4 we illustrate a sub-set of simulated and measured IR-laserlink transmission spectra to facilitate the understanding of the spectral characteristics and the measurement conditions. Individual absorption contributions of the targeted GHGs are well distinguished as is the spectral broadening of the measured spectra, which is due to

- ²⁰ suboptimal detector gain settings during the spectral scanning. A high gain setting was necessary due to the strong atmospheric losses (in particular from beam divergence and molecular absorption), which limited the bandwidth and thus the response of the detector to rapid changes in laser power (for more technical detail see Brooke et al. (2012); correction of this broadening for our purpose is discussed below).
- The simulated total transmission spectra take all GHGs of set X into account, in addition to the absorption due to N₂O and CO. However, these two GHGs are found to have no relevant absorption contribution within the wavenumber ranges of interest; potential influences of such foreign GHGs on the absorption and reference channel transmissions will be discussed later in Sect. 4. The chosen pairs of absorption and



reference channels, marked by dotted lines, evidently fulfill well the requirements for the IR-laser occultation differential transmission principle and therefore allow the basic demonstration of this principle based on the long-path inter-island transmission data. It is evident that a correction for the suboptimal-detector-gain-related spectral broadening

- of the measured spectra will be needed, which will add also to the uncertainty budget. The bottom panel of Fig. 4 illustrates that the CH₄ measurements by laser L3 near 2.3 μm suffered increased signal-to-noise ratio problems, as described by Brooke et al. (2012). The retrieval of CH₄ therefore needs to be expected to be of de
 - graded quality compared to the CO₂ isotope retrievals.
- ¹⁰ In the spectra of Fig. 4 we can furthermore clearly see the broadband contribution of all GHGs to the total absorption and reference channel transmissions of a targeted GHG. However, since we employ the differential transmission principle, the influence of this broadband foreign GHG absorption on the retrieval accuracy is in practice weak or even negligibly small.
- ¹⁵ A good example for such a noticeable influence is provided, for instance, by the influence of H_2O on the two C¹⁸OO-2 channels (top panel); the adjacent H_2O -1 absorption line will leave some residual error in the differential transmission of the C¹⁸OO-2 absorption-reference channel pair. Careful quantification and effective correction of such foreign GHG influences in the selfcalibrating IR-laser occultation retrieved proce-
- ²⁰ dure have been worked out by Schweitzer et al. (2011a) and Proschek et al. (2011). In the context of the experiment data analysis presented here, the quantification of such influences on the retrieval results will be given later in Sect. 4.

3.1.2 Spectral broadening correction

The above-mentioned experiment-specific fact of suboptimal detector gain settings while scanning and recording the spectra (details in Brooke et al., 2012, Appendix A5 therein) led to some artificial broadening of the measured spectral lines, as could already be seen in Fig. 4 and as is more specifically shown in Fig. 5 for three example GHG absorption lines.





In aligning measured and forward-modeled (simulated) transmissions at the absorption channel, the broadening in the measured spectrum becomes visible in the form of a decreased differential transmission between absorption and reference channel in comparison to the forward-modeled spectrum; this difference is marked in Fig. 5

- ⁵ as ΔT_{SC} and serves as spectral correction term in the retrieval to achieve a proper match of forward-modeled and measured differential transmissions. In other words, ΔT_{SC} compensates for the suboptimal detector gain settings during acquisition of the IR-laserlink data files (Table 2) in the course of the experiment. We emphasize that in actual IR-laser occultation measurements such a correction term would not occur, it is just an inadvertent additional effect of this first demonstration experiment (Brooke
- et al., 2012).

The spectral correction term ΔT_{SC} clearly needs to be taken into account in the retrieval process of the campaign data, as it would otherwise bias the GHG results. In order to practically determine ΔT_{SC} for the chosen absorption lines (Table 4), we ap-

plied a moving average filter to the forward-modeled (simulated) spectra such that the resulting filtered and therefore broadened simulated absorption line best-matches the measured absorption line of interest. The difference between the original simulated transmission and the filtered simulated transmission at the reference channel then determines the spectral correction term, as marked in the panels of Fig. 5.

²⁰ For example, for the C¹⁸OO-2 absorption line (upper panel of Fig. 5) a ΔT_{SC} of ~ 0.33 dB is estimated, which results from best-matching the C¹⁸OO-2 absorption line of a measured spectrum, randomly drawn from the subset of measured 4 s spectra (gray lines) in a given IR-laserlink data file, by the broadened C¹⁸OO-2 absorption line of the filtered simulated spectrum. Different absorption lines in different IR-laserlink data files (where adjustments of measurement settings may have occured between acquisitions) may have received different broadening and therefore can lead to different correction terms ΔT_{SC} as is also illustrated by the different panels in Fig. 5.

In practice, the estimation and application of a specific spectral correction term was necessary for all IR-laserlink data files and all chosen absorption lines, not





only because of the changing measurement settings but also because of the broadband wavenumber ranges where the broadening of absorption lines was uneven over the scanned range (for technical details on data acquisition and raw spectra, wavelength calibration, and detector gain and offset issues see Brooke et al., 2012, Appendix A therein). Table 5 lists all spectral correction terms ΔT_{SC} determined, as applicable, for the 19 available data files (Table 2) and the 10 chosen absorption lines (Table 4).

The elaborate matching analysis of filtered-simulated and measured spectra, accompanied by comprehensive sensitivity tests for rough but robust estimation of uncertainties, revealed a reasonable systematic behavior of the spectral broadening effects in the different IR-laserlink data files and their different lasers and wavenumber scan ranges. The different $\Delta \mathcal{T}_{SC}$ values result from the inadvertent broadening process due to detector gain issues having influenced narrow and deep absorption lines in a stronger way than broad and shallow lines. In addition, this "natural" behavior of the filtering can be somewhat perturbed by close neighbor absorption lines as well as near the margins of

10

somewhat perturbed by close neighbor absorption lines as well as near the margins of the scanned wavelength ranges.

In general, as Table 5 shows, the correction terms ΔT_{SC} appear to be stable over data file acquisitions with the same lasers and the same wavelength scan ranges, i.e., when the measurement settings evidently have been (largely) the same. A good example are

the files F2 to F4, and F13 to F16, regarding the three CO₂ isotope absorption lines scanned by laser L2 (first three species columns) as well as the ¹²CO₂ absorption line scanned by laser L1 (seventh species column).

Other data files show similar patterns, also those including narrow wavenumber scan ranges that support a single absorption line only with each given laser, such as files F7

to F10 (cf. Table 2). The ΔT_{SC} uncertainties listed in the caption of Table 5 have been estimated from the spread of the ΔT_{SC} values obtained from using the many individual 4 s spectra in the various data files.

As a specific case, the CH_4 -1|2 correction term values of 1.6 and 0.6 dB were found to be fairly high, given the narrowness and depth of the respective absorption lines.



This is because of the quality of the two CH_4 data files taken towards the very end of the campaign (files F18 and F19), which is clearly degraded compared to all other data files as mentioned above and as reported by Brooke et al. (2012). Therefore, the CH_4 retrieval results have to be treated with caution. More discussion about uncertainty margins follows in Sect. 4.1.

3.2 Retrieval algorithm

The aim of the GHG retrieval in this study is to demonstrate the differential transmission principle, which is the core of the IR-laser occultation processing part of the LMIO method (e.g., Proschek et al., 2011). Therefore, no full spectral fit of the forward¹⁰ modeled spectra to the measured spectra is used, as was done in the initial evaluation of Brooke et al. (2012), but the absorption-reference channel pairs for ten suitable absorption lines, as listed in Table 4, are exploited. Recall that a spaceborne LMIO occultation method, which provides a very fast vertical scan through the atmosphere during an occultation event, would not provide spectra but accurately measured
¹⁵ "monochromatic" data for selected absorption and reference channels (Kirchengast and Schweitzer, 2011).

Given the limited accuracy of the wavemeter and the wavelength calibration in the experiment (Brooke et al., 2012), the absorption line center frequencies of the campaign data do fairly well but not exactly match the nominal line center wavenumber values according to Table 4. The first step of the retrieval was therefore, for each chosen ab-

- sorption line, to search in the measured spectra at the Rx site for the wavenumber of the peak of the targeted absorption line, starting from the nominal wavenumber of the simulated absorption line center, and to extract the corresponding signal amplitude in the Tx and Rx signal, $A_{Abs,Tx}$ and $A_{Abs,Rx}$.
- ²⁵ This was followed by the search for the associated reference channel wavenumber, chosen to be the wavenumber of minimum absorption in the nominal wavenumber interval between the respective reference and absorption channel (cf. Table 4), and extracting at this wavenumber the corresponding signal amplitude, $\mathcal{A}_{\text{Ref,Tx}}$ and $\mathcal{A}_{\text{Ref,Rx}}$.



Typically, these minimum-absorption wavenumbers were found just near the nominal reference wavenumbers, since the nominal wavenumbers had been selected to approximately correspond to the first absorption minimum ("valley") adjacent to the targeted absorption line maximum ("peak") (cf. Fig. 5).

⁵ The signal amplitude and wavenumber values (close to the nominal values) extracted in this way were used in the further retrieval procedure. The relative amplitude \mathcal{A} values, available in units [V/V] in the data files, were converted into units [dB] and used to determine the measured differential transmission for any targeted absorption line, $\Delta \mathcal{T}_{tgt,Meas}$, in the form

¹⁰
$$\Delta \mathcal{T}_{tgt,Meas} = [\mathcal{A}_{Abs,Rx} - \mathcal{A}_{Abs,Tx}] - [\mathcal{A}_{Ref,Rx} - \mathcal{A}_{Ref,Tx}].$$
 (1

The corresponding simulated differential transmissions, $\Delta \mathcal{T}_{tgt,Sim}$, computed at the wavenumbers determined above (doing so at the nominal wavenumbers would not appreciably change the results), were prepared to match these measured transmissions. This was done by employing the RFM model (Dudhia, 2008) within an iterative process to finally determine the desired volume mixing ratios of the target GHGs. The algorithm works as follows.

15

20

As a first step, a 3-D ray tracing from Tx site to Rx site is performed, to determine ray path coordinates in densely sampled along-ray steps (100 m spacing). Within this process, the refractivity is calculated by use of the modified Edlen-formula, which was also applied by Proschek et al. (2011). The atmospheric conditions along the ray are taken from the ECMWF analysis fields, interpolated to the start time of any data file for all spectra in the file. Sensitivity tests showed that there was no need to repeatedly

compute the ray path for 4 s spectra individually, since the variations in pressure (p) and temperature (T) are very small over the short time frame of a data file so that the

²⁵ initial ray path does not change appreciably (for more information on the estimated uncertainty in *p* and *T* themselves see Sects. 2.2 and 4.4). The ECMWF values of *p*, *T*, and H₂O (derived from the humidity) obtained along the ray path were then stored for later usage in the iterative GHG retrieval, which was done for all 4 s spectra of a file.



The iterative retrieval needs reasonable initial values for the targeted GHGs as well as for some background GHGs that may have a small influence on the selected absorption and reference channels. We chose the along-ray averaged H_2O value from ECMWF as initial/background value for H_2O , and the CO_2 , CH_4 , N_2O , and CO values from FASCODE (FASCODE, 2008), as quoted in Sect. 2, as initial/background values for these well-mixed GHGs. The foreign-species influence of CO is only relevant to CH_4 and very small in (transmission effected within 0.01 dB), so the somewhat less well-mixed character of this species is not relevant here and we can as well use the fixed FASCODE value for its initialisation. All target GHGs, determined as ray-pathaveraged volume mixing ratios \overline{v}_{tot} , are utilized in units ppmv.

The iteration process uses the atmospheric parameters and initial/background GHG values and – for any chosen GHG absorption line (Table 4) in a data file – includes at each iteration step *i* the simulation of along-ray transmissions for absorption and reference channel, $\mathcal{T}_{Abs,Sim;i}$ and $\mathcal{T}_{Ref,Sim;i}$, as well as of the ray-averaged absorption cross section, $\bar{\sigma}_{tgt}$, employing the RFM model (Dudhia, 2008). The iteration itself is a simple and robust Newton iteration over target GHG volume mixing ratio, $\overline{\mathcal{V}}_{tgt;i}$, starting with an initial value $\overline{\mathcal{V}}_{tgt;0}$ and being iteratively updated proportional to a residual differential transmission increment $\Delta[\Delta \mathcal{T}_{tat;i}]$. In particular, the algorithm is formulated as

11611

$$\overline{\mathcal{V}}_{\text{tgt};i+1} = \overline{\mathcal{V}}_{\text{tgt};i} - \frac{c_{\text{dB2\%}} \cdot \mathcal{R} \cdot \overline{T} \cdot \Delta[\Delta \mathcal{T}_{\text{tgt};i}]}{\overline{\rho} \cdot \overline{\sigma}_{\text{tgt}}(\overline{T}, \overline{\rho}, \overline{\mathcal{V}}_{\text{tgt};i}) \cdot L_{\text{TxRx}}},$$

20 where

$$\Delta[\Delta \mathcal{T}_{tgt;i}] = \Delta \mathcal{T}_{tgt,Sim;i} - \Delta \mathcal{T}_{tgt,Meas},$$
 with

$$\begin{split} & \Delta \mathcal{T}_{\text{tgt,Sim};i} = \mathcal{T}_{\text{Abs,Sim};i} \left(\mathcal{T}, p, \overline{\mathcal{V}}_{\text{tgt};i} \right) \\ & - \mathcal{T}_{\text{Ref,Sim};i} \left(\mathcal{T}, p, \overline{\mathcal{V}}_{\text{tgt};i} \right) - \Delta \mathcal{T}_{\text{SC,tgt}}. \end{split}$$

Discussion Paper AMTD 7, 11593–11652, 2014 **Retrieval and** validation of greenhouse gases **Discussion** Paper for the Canary **Islands** experiment V. Proschek et al. **Title Page** Abstract Introduction **Discussion** Paper Conclusions References Tables Figures Back Close **Discussion** Paper Full Screen / Esc Printer-friendly Version Interactive Discussion

(2)

(3)

(4)

In this set of equations, $\Delta T_{SC,tgt}$ (in dB) is the spectral correction term that accounts for the spectral broadening explained in Sect. 3.1.2. It enables the simulated target GHG differential transmission $\Delta T_{tgt,Sim;i}$ (in dB) to nominally match the measured differential transmission $\Delta T_{tgt,Meas}$ (in dB), in order to produce an adequate residual increment $\Delta [\Delta T_{tgt;i}]$ (in dB). \overline{T} (in K) and \overline{p} (in Pa) are the ray-averaged temperature and pressure, respectively, $c_{dB2\%} = 23.026 \% dB^{-1}$ is the conversion factor from units dB to

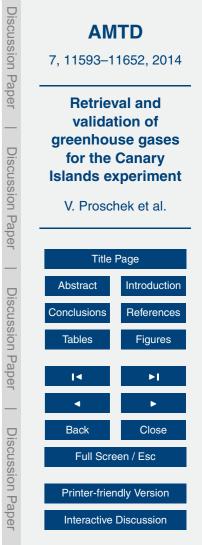
units %, $\mathcal{R} = 8.3145 \,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ is the molar gas constant, $\bar{\sigma}_{tgt}$ (in m² mol⁻¹) is the target GHG molar cross section at the absorption line center, and L_{TxRx} (in m) is the ray path length from Tx to Rx.

¹⁰ We found that this iterative algorithm converges fast within a few iterations (seven at most); we terminated it when the residual relative change in the volume mixing ratio, $100 \cdot \frac{|\overline{v}_{tgt;i+1} - \overline{v}_{tgt;i}|}{\overline{v}_{tgt;i}}$, was smaller than 0.05% or when ten iteration steps did not lead to convergence (the latter occured only in rare cases of problematic spectra, however, for which the results generally ended as outliers). The final iteration results for \overline{v}_{tgt} were stored as the retrieved GHG values. They are discussed in terms of their uncertainty and their consistency with the independent validation data in the next sections.

4 Retrieval uncertainty analysis

5

We now discuss the uncertainties estimated for the retrieval results, the GHG volume mixing ratios \mathcal{V} , and their different origins. There are several influences which are of a mixed systematic and random nature. Table 6 lists all of them for the ten selected absorption species peaks. The estimated uncertainties $\Delta \mathcal{V}$ include uncertainties due to the limited accuracy of the spectral correction term $\Delta \mathcal{T}_{SC}$ and of the spectroscopic parameters as well as due to the limited knowledge of atmospheric water vapor (H₂O) concentration and of pressure and temperature (Table 6). The underlying sources of these four types of uncertainty are essentially independent so that the resulting





combined uncertainty can be computed as a root-mean-square sum of the four uncertainties.

The combined uncertainties (rightmost column of Table 6) for the CO_2 isotopes amount to about 11 to 14%, and are dominated by the spectroscopic uncertainties.

- ⁵ For comparison, the initial example CO₂ retrieval performed by Brooke et al. (2012) led to an uncertainty estimate of about 4 %, but this value included neither the spectroscopic uncertainty (even if it was discussed in the text) nor the spectral-correction-term uncertainty (as they did a spectral-fit retrieval rather than a differential transmission retrieval from absorption-reference channel pairs). If we excluded these two uncertainty
- ¹⁰ sources, the current uncertainty estimate from our differential transmission retrieval process would still be somewhat more conservative (about 6%), since we found somewhat higher values for the uncertainties due to H_2O concentration, *p*, and *T* from our more detailed analysis.

The combined H_2O uncertainty is about 51 %, strongly governed by the uncertain H_2O knowledge from the validation data. Finally, the combined CH_4 -1 uncertainty is about 22 %, dominated by spectroscopic uncertainty, while the combined CH_4 -2 uncertainty is about 10 %, dominated by the uncertainty in the spectral correction term.

The individual uncertainty contributions are briefly explained separately in the following subsections, followed by a discussion of the complementary estimation of the statistical uncertainty from the measurements. The latter was estimated, within aver-

aging periods of about 10 min, based on the ensemble of retrieved GHG values (from the individual 4 s spectra) falling into each such period.

4.1 Uncertainty due to the spectral correction term

The uncertainty $\Delta \mathcal{V}$ in the spectral correction term takes into account the uncertainty transferred into the volume mixing ratio from the uncertainty (spread) of the $\Delta \mathcal{T}_{SC}$ values obtained when best-matching individual 4 s spectra within an IR-laserlink data file to the corresponding filtered-simulated spectrum of the file. Details of the $\Delta \mathcal{T}_{SC}$ estimation have been described in Sect. 3.1.2 above, and the best-estimate values and their



corresponding uncertainties $\Delta(\Delta T_{SC})$ have been listed in Table 5 and its caption. These uncertainties $\Delta(\Delta T_{SC})$ are the basis for estimating the corresponding uncertainties ΔV for all targeted absorption lines, shown in Table 6.

The relation between $\Delta \mathcal{V}$ and $\Delta(\Delta \mathcal{T}_{SC})$ is essentially a linear one as visible from the ⁵ right-hand-side term of Eq. (2) above, where one sub-term within $\Delta(\Delta \mathcal{T}_{tgt})$ is $\Delta(\Delta \mathcal{T}_{SC})$. We used this right-hand-side term of Eq. (2) to estimate the linear transfer function from $\Delta(\Delta \mathcal{T}_{SC})$ to $\Delta \mathcal{V}$ for all species' absorption peaks. Figure 6 shows example results for CO₂ isotope lines, where the linear solid lines indicate the relation that somewhat varies due to the different underlying atmospheric conditions and absorption cross sections of different spectra (spread of lines with same color). Cross-check with real GHG retrieval

- ¹⁰ different spectra (spread of lines with same color). Cross-check with real GHG retrieval results based on Eqs. (2)–(4), using intentional relative changes $\Delta(\Delta T_{SC})$ of +20, +30, and +40 % against the best-estimate ΔT_{SC} , quite well confirmed the linear relation and the spread (color-filled circles in Fig. 6).
- Therefore, we used these linear transfer functions to conservatively estimate $\Delta \mathcal{V}$ from $\Delta(\Delta \mathcal{T}_{SC})$, in the sense that we used, for any absorption peak of Table 6, the highest applicable $\Delta(\Delta \mathcal{T}_{SC})$ value from the caption of Table 5 (vertical dotted lines in Fig. 6) and then estimated the corresponding $\Delta \mathcal{V}$ value to be the one associated with the steepest linear transfer function among the bundle of functions evaluated for a given peak (horizontal dotted lines in Fig. 6, indicating the resulting $\Delta \mathcal{V}$ on the *y* axis).
- The spectral-correction-term uncertainties summarized in Table 6 (second column) were all estimated in this way and their typical range is from about 4 to 8 %. Clearly, a follow-on experiment should aim at avoiding this uncertainty component by optimized control and documentation of experiment settings and an improved signal-to-noise ratio at the receiver.

25 4.2 Uncertainty due to spectroscopic parameters

The uncertainty in the spectroscopic parameters is estimated on the basis of the uncertainties given by the HITRAN08 database (Rothman et al., 2009). The most relevant contributing uncertainties have been shown in Table 4 and include the uncertainty in





the line intensity, ΔS , and in the air-broadened half width, $\Delta \gamma_{air}$. Their contribution to the computation of simulated absorption lines can be seen from the detailed equations in Appendix A2 of Rothman et al. (1998), which shows that these two uncertainties dominate (see also the results of Harrison et al., 2011). We therefore use these two uncertainties ΔS and $\Delta \gamma_{air}$ as the basis for the spectroscopic uncertainty that will also contribute to the combined volume mixing ratio uncertainty $\Delta \mathcal{V}$.

Based on the results of and experience from many sensitivity studies in the Harrison et al. (2011) work, we assume a roughly linear relation between the spectroscopic uncertainty and $\Delta \mathcal{V}$, reflecting also that the uncertainties in line intensity and air-broadened half width generally do not add linearly but partially compensate each

other in $\Delta \mathcal{V}$. On the basis of these assumptions we adopted as spectroscopic uncertainty estimates in Table 6 (third column) a reasonable trade off value of the upper and lower margin uncertainty estimates from HITRAN08 according to Table 4.

10

In particular, for the CO₂ isotopes we adopted an uncertainty of 10 % (the ΔS lower

- ¹⁵ and $\Delta \gamma_{air}$ upper margin) and for H₂O 8% (near the ΔS upper margin, given that $\Delta \gamma_{air}$ is quoted to be accurate to within 1 to 2% for these lines in HITRAN08). For CH₄-1 we adopted an uncertainty of 20% (dominated by the respective $\Delta \gamma_{air}$ uncertainty quoted in HITRAN08 to be at least 20%) and for CH₄-25% (upper margin of ΔS and $\Delta \gamma_{air}$ for this line).
- It is clear that these uncertainty estimates are educated guesses only rather than detailed quantitative estimates. However, given the coarseness of the uncertainty specifications in HITRAN and the unknown sign of the errors in the spectroscopic parameters as well as the first-time nature of the IR-laserlink experiment evaluated in this study, we do not consider it worthwhile to explore this uncertainty in a more refined manner
- for the current purpose. Rather we strongly recommend, underscoring the conclusions of Harrison et al. (2011), that the current spectroscopic knowledge on the selected lines for the ACCURATE/LMIO mission concept should be substantially improved by new highly accurate laboratory spectroscopy, to meet the ACCURATE spectroscopic





accuracy requirements (Kirchengast and Schweitzer, 2011; Harrison et al., 2011). This could reduce spectroscopic uncertainty in a follow-on experiment to smaller than 0.2%.

4.3 Uncertainty due to water vapor

In Sect. 2.2 and Fig. 2 we showed that the water vapor volume mixing ratio in the CRDS validation data exhibited a comparatively small variation of ~ 0.1% during the measurement times at the Rx site, while it varied from about 0.2 to 0.8% at the Tx site. Furthermore, the along-ray water vapor from ECMWF showed volume-mixing-ratio variations within about 0.1 to 0.5% (Fig. 3), which is comparable with the CRDS ranges. In order to account for these considerable variations we adopted a large uncertainty of ±50% regarding the knowledge of H₂O along the IR-laserlink (reflecting a "2-sigma

range" from < 0.1 to 0.6% if assuming a central value of 0.3%, roughly covering the variability).

Table 6 (fourth column) shows that this limited knowledge available on H₂O from the campaign (uncertainty 50%) strongly governs the combined uncertainty attributed to the H₂O retrieval results. The validation for this highly variable species will therefore only allow for very broadly checking of the consistency of the retrieved data with the validation data.

On the other hand, despite the need of assuming such a high uncertainty on the H_2O volume mixing ratio, the absorption lines of the CO_2 isotopes and of CH_4 are found to ²⁰ be very weakly sensitive to this uncertainty, since the H_2O foreign-species influence on these absorption lines is very small (see Table 6 fourth column). Moreover, the effect of H_2O on the IR refractivity is smaller than 0.1 % (e.g., Schweitzer et al., 2011a) so that also the ray path knowledge is essentially not influenced by the H_2O uncertainty.

Retrieval computations for sensitivity testing that assume an H₂O uncertainty of $\pm 50\%$ confirm that the uncertainties $\Delta \mathcal{V}$ induced in retrieved CO₂ isotopes and CH₄ are generally in the range of about 0.5 to 4% only, much smaller than the spectral-correction-term and spectroscopic uncertainties. The estimates in Table 6 (fourth column) for the CO₂ and CH₄ lines are from such computations. The least sensitive line



is CH₄-2 (0.3%), the most sensitive one C¹⁸OO-2 (6%). The latter line well illustrates that the major source of this uncertainty is the residual differential foreign-species influence of H₂O on the absorption and reference channels (compare the H₂O spectrum in Fig. 4, upper panel, near the C¹⁸OO-2 peak).

⁵ Related to a follow-on experiment we can learn from these uncertainty estimates that an effort to provide H_2O validation data to within an accuracy of 5% (representative along the IR-laserlink, e.g., from a co-aligned microwave link with suitable frequencies near 23 GHz, as part of the LMIO method) would enable this uncertainty component to be constrained to less than 0.2 and 0.5% in CO_2 and CH_4 retrievals, respectively.

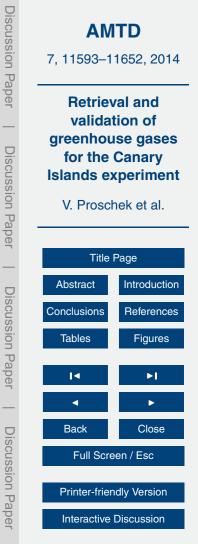
10 4.4 Uncertainty due to pressure and temperature

Since atmospheric pressure and temperature play a role in the ray path simulation and the iteration process to calculate \mathcal{V} (Eqs. 2 to 4), the contribution of their measurement uncertainty, estimated to be 1 % (see Sect. 2.2, Fig. 2), to the retrieval uncertainty $\Delta \mathcal{V}$ must also be investigated.

¹⁵ Regarding their influence on the ray path trajectory, we found that the effects of the 1 % uncertainty in *p* and *T* are essentially negligible; the induced deviation of ray paths at the tangent point altitude (mid-way along the ray from Tx to Rx) is smaller than 2 m. For estimating their influence on \mathcal{V} within the iterative retrieval process (Eqs. 2 to 4), we performed sensitivity testing by retrievals with all combinations of ±1 % *p* error and ±1 % *T* error. Taking for each species peak the highest (most conservative) uncertainties from these results yielded the estimates $\Delta \mathcal{V}$ summarized in Table 6 (fifth column).

It can be seen that ¹³CO₂, C¹⁸OO, and CH₄ are only linearly sensitive and therefore exhibit a p/T-induced uncertainty ΔV of no more than 1 %, while the ¹²CO₂ and

 $_{25}$ H₂O lines react more sensitively with 6 and 3.5%, respectively. These different p/T-sensitivities of different lines are mainly related to the quantum-mechanical state transitions of the lines (Schweitzer, 2010; Kirchengast and Schweitzer, 2011).





For a follow-on experiment it will be desirable to constrain the p and T knowledge along the ray to ~ 1 hPa and ~ 0.3 K (e.g., by complementing the Tx and Rx p, T measurements by several high-accuracy radiosonde launches beneath the ray path or balloon measurements near the ray path). This would reduce this uncertainty component to less than 0.2 to 0.5 % in the GHG retrievals.

4.5 Statistical uncertainty in the measurements

We now discuss statistical uncertainties estimated from the retrieved GHG data, including outlier rejection as a quality control process, in order to get a complementary view of the consistency of our results, i.e., complementary to the component-wise uncertainty estimation discussed above that aims at providing an "outer envelope" to all systematic and random uncertainties. The statistical uncertainties estimated here for the various species aim at finding out, under the assumption of random errors that can be reduced by averaging over individual retrieval results, how well the median and percentile estimates obtained can represent the validation data. In particular, we used averaging periods of about 10 min and determined medians and percentiles based on the ensemble of retrieved GHG values from the individual 4s spectra falling into any such period.

More precisely, the first step of our statistical analysis is a quality control and outlier rejection, i.e., we aim to isolate those individually retrieved GHG values from the en-

- ²⁰ semble in any averaging period that derive from 4 s spectra of bad quality. To this end, we performed a first calculation of the median (representing the "mean"), and a calculation of the 16 and 84%-percentiles (representing a 68% " $\pm 1\sigma$ " range), from all individual retrievals of an IR-laserlink data file over a period of at least 10 min if possible (maximum 15 min, and less, if the data file or the rest of data file is shorter than
- ²⁵ 10 min). Based on this output, all individual retrievals outside of the " $2.5 \cdot (\pm 1\sigma)$ " range were rejected. Subsequently, as second step, we re-calculated the median and the 16 and 84 %-percentiles from the remaining subset of individual retrievals, providing the final estimates of the "mean" and the " $\pm 1\sigma$ " range for the given ~ 10 min period.



Figure 7 illustrates this method for a couple of example ~ 10 min periods for several ${}^{12}CO_2$, H₂O, and CH₄ lines; the characteristics of all other retrieval ensembles look similar. The retrieval results are shown as a function of the underlying measured differential transmission values (Eq. 1) that flow into the retrieval algorithm (Eqs. 2 to 4). Given the near-linearity of the algorithm, the resulting individual retrievals exhibit a near-linear dependence on the size of the measured ΔT values.

All panels of Fig. 7 confirm that the retrieval ensembles in each ~ 10 min period clearly cluster around a certain average and are associated with a certain spread (" $\pm 1\sigma$ " range) that arises from measurement errors in the individual 4 s spectra and influences of other uncertainties discussed above. Assuming the deviations from the average to be random, the measurement uncertainty of the ~ 10 min averages is estimated by the " $\pm \sigma/\sqrt{n}$ " range. The degree of consistency of this comparatively narrow uncertainty with the validation data is of particular interest as a pointer to potential biases in the data (e.g., from spectroscopic parameter uncertainties or technical mea-

The ¹²CO₂ data clustering and average indicate a nearly unbiased behavior (biases of ~ 1 %), while the H₂O data clustering and average look of similar quality but the large uncertainty range of the reference data allows no inferences on the biases. The " $\pm 1\sigma$ " range for both species is of the order of 5 to 10 %, somewhat smaller than the combined uncertainty estimates above, which is meaningful as this spread does not reflect systematic uncertainties and validation-data uncertainties (in case of H₂O).

The clustering and the average of the CH_4 ensemble (bottom panel) indicate that these measurement data had bias problems, since both clusters (red and blue) appear to be located systematically below the "true" CRDS reference value (green line). This is consistent with the CH measurement problems pointed out by Procket et al. (2012)

²⁵ is consistent with the CH₄ measurement problems pointed out by Brooke et al. (2012). While Brooke et al. (2012) refrained for this reason from any CH₄ retrieval attempts, this result here still indicates that basically also the CH₄ spectra from the long-path measurements have been physically sound although not of sufficient quality for quantitative consistency with accurate validation data.





The results from all $\sim 10 \text{ min}$ periods, based on all data files and inspecting all species analyzed, are discussed in the next section, where only the combined uncertainties and the measurement uncertainty of the $\sim 10 \text{ min}$ averages are visualized together with the reference data, to enable a synthesis view.

5 Retrieval results and validation

The results from the analysis of the entire measured dataset from all available data files, as summarized in Table 2, turn out to provide a successful first proof-of-concept of long-path IR-laser occultation measurements using the differential transmission principle as applied in the ACCURATE/LMIO mission concept. Figures 8 and 9 show the complete set of results from the two successful campaign nights 20 to 21 July and 21 to 22 July 2011. Reliable results have been obtained for all three targeted CO₂ isotopes (${}^{12}CO_2$, ${}^{13}CO_2$, $C^{18}OO$), H₂O, and CH₄.

The retrieval results for the three CO_2 isotopes (upper three panels of Fig. 8, one per isotope) exhibit reliable repeatability of the retrieval results, for all species absorption lines exploited (Table 4). The average (median) values of the ~ 10 min periods are generally found to lie within 2% of the CRDS reference data, which themselves are consistent with narrow uncertainty of < 1% with the sampling flask cross-check measurements. We note that the isotopic abundance factors for calculating the isotope concentrations from the total CO_2 concentration were taken from the HITRAN08 database, both for the retrieval results and the CRDS and flask reference data shown (for more information on up-to-date mole fractions and isotopic abundance factors for

 CO_2 isotopes see Coplen et al. (2002) and Chen et al. (2010); the differences to the HITRAN08 values are negligible for the purposes of this study).

The combined uncertainties (red "error bars") are shown according to Table 6 and ²⁵ indicate that within the uncertainty, all CO₂ retrieval results are consistent with the CRDS reference data (green filled circles). The statistical uncertainty of the averages (black "error bars") is significantly smaller than the combined uncertainty and

11620



particularlynarrow in case of a large ensemble size in a given ~ 10 min period. This can be seen when comparing the results at certain times in Fig. 8 with the number of spectra in the data files available at those times (see Table 2). Likewise, the cases for which the average values (medians; red filled circles) deviate more than about 2 % from

- the reference values are usually associated with small ensemble sizes so that also the statistical uncertainty of these averages is usually higher for these cases. A few cases show narrow statistical uncertainty despite of stronger biases against the reference (e.g., the C¹⁸OO retrievals near 0:30 h on 22 July); in these cases the measured spectra have been of poorer quality, typically from degraded signal-to-noise ratios.
- The retrieval results for H₂O (bottom panel of Fig. 8) show similar stability and narrow statistical uncertainty as the CO₂ results, but the IR-laserlink representation uncertainty of the CRDS reference data (light gray-shaded area) and the ECMWF reference data (gray-shaded area) is much larger, exceeding the uncertainty range estimated for the H₂O retrievals. The reason for that is the high horizontal variability of water vapor as shown in Fig. 3 and described in Sect. 2.2. Under these broad uncertainties, we find the H₂O retrieval results to be consistent with the reference data. However, under these

circumstances, it is a a fairly weak validation in quantitative terms.

Figure 9 shows the results for the CH_4 retrievals within the final measurement period in the morning of 22 July 2011, where altogether just three ~ 10 min periods are available, acquired around 06:00 UTC. As discussed in Sect. 4, and already visible in the

- ²⁰ able, acquired around 06:00 01C. As discussed in Sect. 4, and already visible in the example clusters of CH_4 results shown in the bottom panel of Fig. 7, the CH_4 retrieval averages (medians; orange filled circles) exhibit a negative bias of about –10 to –15% compared to the CRDS reference data. The latter agree very well (to within < 1%) with the independent flask measurements taken about 2 h before (near 04:00 UTC).
- ²⁵ The estimated combined uncertainty (orange error bars) according to Table 6 does cover the reference data in only one of the three retrieval cases, signaling the more fundamental nature of the bias in the CH₄ measurements as pointed out by Brooke et al. (2012) and in Sect. 4. The one case covering the reference data is doing so only because of the high estimated spectroscopic uncertainty of the CH₄-1 absorption



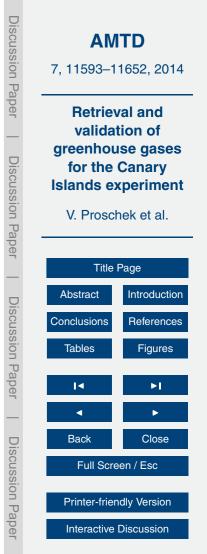


line. The quite narrow statistical uncertainty ranges of the averages are far from covering the reference data. However, even though the CH_4 results are in this way found to be quantitatively inconsistent within the uncertainties with the validation reference data, these somewhat biased results are still physically sound and indicate that equal measurement quality such as for CO_2 would have led to consistency.

6 Summary and conclusions

In this study we provided a detailed analysis of a pioneering proof-of-concept experiment: a ground-based IR-laser link over 144 km between the two Canary Islands La Palma and Tenerife was used to validate the differential transmission principle for longpath GHG measurements as proposed for spaceborne IR-laser occultation (Kirchengast and Schweitzer, 2011). Following the experiment introduction and initial analysis of a few sample spectra by Brooke et al. (2012), we analyzed and validated the entire IR-laser link dataset acquired during two successful campaign nights of 21 and 22 July 2011. Complementary independent data, comprised of weather station data, high-resolution ECMWF analysis fields, and CRDS and sampling flask GHG measurements, which had been acquired during the campaign at the Tx and Rx locations, served as reference data for evaluation and validation of the IR-laserlink results.

We first introduced the pre-processed IR-laserlink data and the validation datasets, followed by a description of the data processing setup and the differential transmission based retrieval algorithm. We presented GHG volume mixing ratio results for the three main CO₂ isotopes (¹²CO₂, ¹³CO₂, C¹⁸OO) as well as for H₂O and CH₄. Furthermore, we performed a thorough retrieval uncertainty analysis, where we accounted for the following uncertainties: (i) uncertainties from a spectral correction, needed due to in-advertent spectral line broadening in the campaign measurements that occured due to suboptimal Rx detection settings as discussed by Brooke et al. (2012) (ii) uncertainty from spectroscopic parameters uncertainties due to limited accuracy of HITRAN08 pa-





rameters, especially of line intensity and air-broadened halfwidth, (iii) uncertainty from

atmospheric parameters, due to limited accuracy of atmospheric pressure, temperature, and H_2O , in the retrieval and validation. The results for the CO_2 isotopes, H_2O , and CH_4 were then validated against the CRDS and flask reference data, for assessing their quality and consistency with these accurate and proven data.

The following main conclusions can be drawn.

5

10

15

20

25

- 1. We found the IR-laserlink retrieval results for all three CO_2 isotopes and for H_2O robust and repeatable, and the retrieval results are consistent within uncertainties with the CRDS and flask reference data. The $CO_2 \sim 10$ min averages were generally consistent within ~ 2% with the reference data, while the high horizontal variability of H_2O led to broad uncertainties (of the order of 50%) in the intercomparison, enabling for this species only a weak validation. For CH_4 , for which only a few campaign measurements existed, we found the results similarly robust and repeatable as for the other species but somewhat biased (about -10 to -15%) against the reference data. This confirms the specific measurement problems pertaining to the CH_4 spectra as discussed by Brooke et al. (2012).
- 2. The estimated combined uncertainty in the retrieval results from spectral correction, spectroscopic parameters, limited H_2O knowledge, and pressure and temperature uncertainties, was generally found in the range of about 10 to 14 % (except for H_2O , which is dominated by limited H_2O variability knowledge, and for one CH_4 absorption line with larger spectroscopic uncertainty). This estimated uncertainty is primarily dominated by the spectroscopic uncertainty (in HITRAN08 line parameters), followed by the spectral correction uncertainty being second-most important for the majority of the species absorption lines used. There is significant room to reduce these first-time-experiment uncertainties in a more consolidated follow-on experiment (to < 0.2 to 0.5 %) as summarized in the outlook below.
- Considering these first long-path IR-laserlink demonstration results for the GHGs carbon dioxide, methane, and water vapor – and the related understanding and insight established by this study – from an overall perspective, we can conclude



that the July 2011 Canary Islands experiment was definitely successful in demonstrating the feasibility of monitoring GHGs in the free atmosphere by IR-laser occultation employing the differential transmission principle. The ACCURATE/LMIO mission concept (Kirchengast and Schweitzer, 2011) thus has a sound basis in this respect.

As an outlook to next steps, in particular to a more consolidated ground-based or airborne follow-on experiment, the main priorities for improvements of the experiment include a reduction of uncertainties in all components of the combined uncertainty budget and use of improved Tx and Rx technologies.

5

- ¹⁰ Regarding the uncertainties, spectral correction uncertainties can be reduced to < 0.1 % by optimized control of experiment settings and an improved signal-to-noise ratio at the Rx. Spectroscopic uncertainties can be reduced to < 0.2 % by dedicated high-accuracy laboratory spectroscopy for targeted absorption lines (Kirchengast and Schweitzer, 2011; Harrison et al., 2011). Uncertainties due to limited H₂O knowledge
- can be reduced to < 0.2 to 0.5 % by providing H₂O validation data to within an accuracy of 5 % for the IR-laser link (e.g., from a co-aligned microwave link with suitable frequencies near 23 GHz, such as being part of the LMIO method). Pressure and temperature uncertainties can be reduced to < 0.2 to 0.5 % by ensuring an accuracy of ~ 1 hPa and ~ 0.3 K along the link (e.g., by complementing the Tx and Rx atmospheric data by several radiosonde launches or balloon-borne observations). Overall, this implies that
- a follow-on experiment should constrain the combined uncertainty of GHG retrievals to smaller than 0.5%, enabling to rigorously prove also the accuracy and stability of IR-laser occultation.

Regarding improved technologies, the use of more accurate wavemeters (highaccuracy frequency stabilization) and somewhat amplified IR-laser signals (to a few 100 mW) at the Tx, of a (semi-)automatic pointing and tracking system for the Tx-to-Rx laserlink, and of a more elaborated multi-channel detection system at the Rx, will enable the achievement of the narrow uncertainty budget of < 0.5 % from the technology side.





Preparations in both directions, uncertainty reduction and technology improvement, are on-going. Given the encouraging results of the first-time experiment reported in this study it is hoped that a more rigorous follow-on experiment will be conducted within the next two years. This will constitute a vital further step, among others, towards a full spaceborne realization of an ACCURATE/LMIO mission.

Acknowledgements. The July 2011 Canary Islands experiment, providing the basis for this study, was funded by the European Space Agencey's Support to Science Element (STSE) and supported by the Earth Observation Future Missions program, including use of ESA's OGS facility. All contributors beyond the authors of this study are thanked for their support to this experiment, including the surgery and ensure of the Northern Onticel Telescope (NOT) for elleving

- iment, including the owners and operators of the Northern Optical Telescope (NOT) for allowing the use of their facilities. RFM and FASCODE were provided by A. Dudhia (Univ. of Oxford, UK) via http://www.atm.ox.ac.uk/RFM, HITRAN was provided by L. Rothman (Harvard Univ., USA) via http://www.cfa.harvard.edu/hitran, and atmospheric analysis fields were made accessible by the ECMWF (Reading, UK). Local meteorological data were obtained at the Tx site from
- the NOT weather station via http://www.not.iac.es/weather/ and at the Rx site from the Global Oscillation Network Group (GONG) weather station via http://www.iac.es/weather/otdata/. This research, including development work on the simulation and data processing integrated within the xEGOPS/EGOPS system, was funded by ESA under the ACTLIMB, IRDAS, IRDAS-EXP, and AEXPWIND studies and partially by FFG-ALR (Austria) under the ACCU-Clouds study.

20 **References**

Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goed, A. P. J.: SCIAMACHY: mission objectives and measurement modes, J. Atmos. Sci., 56, 127–150, doi:10.1175/1520-0469(1999)056<0127:SMOAMM>2.0.CO;2, 1999. 11596

²⁵ Brailsford, G. W., Stephens, B. B., Gomez, A. J., Riedel, K., Mikaloff Fletcher, S. E., Nichol, S. E., and Manning, M. R.: Long-term continuous atmospheric CO₂ measurements



at Baring Head, New Zealand, Atmos. Meas. Tech., 5, 3109–3117, doi:10.5194/amt-5-3109-2012, 2012. 11596

- Brooke, J. S. A., Bernath, P. F., Kirchengast, G., Thomas, C. B., Wang, J.-G., Tereszchuk, K. A., González Abad, G., Hargreaves, R. J., Beale, C. A., Harrison, J. J., Schweitzer, S.,
- ⁵ Proschek, V., Martin, P. A., Kasyutich, V. L., Gerbig, C., Kolle, O., and Loescher, A.: Greenhouse gas measurements over a 144 km open path in the Canary Islands, Atmos. Meas. Tech., 5, 2309–2319, doi:10.5194/amt-5-2309-2012, 2012. 11597, 11598, 11599, 11603, 11605, 11606, 11607, 11608, 11609, 11613, 11619, 11621, 11622, 11623
- Chahine, M. T., Pagano, T. S., Aumann, H. H., Atlas, R., Barnet, C., Blaisdell, J., Chen, L., Divakarla, M., Fetzer, E. J., Goldberg, M., Gautier, C., Granger, S., Hannon, S., Irion, F. W.,
- vakarla, M., Fetzer, E. J., Goldberg, M., Gautier, C., Granger, S., Hannon, S., Irion, F. W., Kakar, R., Kalnay, E., Lambrigsen, B. H., Lee, S.-Y., Le Marshall, J., McMillan, W. W., McMillin, L., Olsen, E. T., Revercomb, H., Rosenkranz, P., Smith, W. L., Staelin, D., Strow, L. L., Susskind, J., Tobin, D., Wolf, W., and Zhou, L.: AIRS: improving weather forecasting and providing new data on greenhouse gases, B. Am. Meteorol. Soc., 87, 911–926, doi:10.1175/BAMS-87-7-911. 2006. 11596
- Chalon, G., Cayla, F., and Diebel, D.: IASI: an advanced sounder for operational meteorology, in: Proc. 52nd Int. Astronautical Congress, 1–9, available at: http://smsc.cnes.fr/

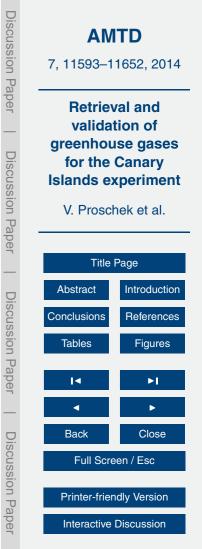
30

documentation/IASI/Publications/PRESENTATION_IAF_2001.pdf, 2001. 11596

Chen, H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D.,
 Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO₂ and CH₄) using the cavity ring-down spectroscopy (CRDS) technique, Atmos. Meas. Tech., 3, 375–386, doi:10.5194/amt-3-375-2010, 2010. 11620

Coplen, T. B., Böhlke, J. K., De Bièvre, P., Ding, T., Holden, N. E., Hopple, J. A., Krouse, H. R., Lamberty, A., Peiser, H. S., Révész, K., Rieder, S. E., Rosman, K. J. R., Roth, E., Tay-

- lor, P. D. P., Vocke, R. D. J., and Xiao, Y. K.: Isotope-abundance variations of selected elements, Pure Appl. Chem., 74, 1987–2017, doi:10.1351/pac200274101987, 2002. 11620
- Desjardins, R. L., MacPherson, J. I., Schuepp, P. H., and Karanja, F.: An evaluation of aircraft flux measurements of CO₂, water vapor and sensible heat, Bound.-Lay. Meteorol., 47, 55–69, doi:10.1007/BF00122322, 1989, 11596
- Dudhia, A.: Reference Forward Model RFM: Inst. of Atmos., Oceanic and Planet. Phys., Univ. of Oxfor, Oxford, UK, available at: http://www.atm.ox.ac.uk/RFM/ (last access: 13 November 2014), 2008. 11604, 11610, 11611





FASCODE: RFM Website – FASCODE Model Atmospheres: Inst. of Atmos., Oceanic and Planet. Phys., Univ. of Oxford, Oxford, UK, available at: http://www.atm.ox.ac.uk/RFM/atm (last access: 13 November 2014), 2008. 11604, 11611

From, E. and Keeling, C. D.: Reassessment of late 19th century atmospheric carbon dioxide

- variations in the air of western Europe and the British Isles based on an unpublished analysis of contemporary air masses by G. S. Callendar, Tellus B, 38, 87–105, doi:10.1111/j.1600-0889.1986.tb00092.x, 1986. 11596
 - Gorbunov, M. E. and Kirchengast, G.: Fluctuations of radio occultation signals in X/K band in the presence of anisotropic turbulence and differential transmission retrieval performance, Radio Sci., 42, RS4025, doi:10.1029/2006RS003544, 2007. 11596

10

- Gurk, Ch., Fischer, H., Hoor, P., Lawrence, M. G., Lelieveld, J., and Wernli, H.: Airborne insitu measurements of vertical, seasonal and latitudinal distributions of carbon dioxide over Europe, Atmos. Chem. Phys., 8, 6395–6403, doi:10.5194/acp-8-6395-2008, 2008. 11596 Hamazaki, T., Kaneko, Y., and Kuze, A.: Carbon dioxide monitoring from the GOSAT satellite,
- in: Proceedings of the XXth ISPRS Conference, 1–3, available at: http://http://www.isprs.org/ proceedings/XXXV/congress/comm7/papers/43.pdf, 2004. 11596
 - Harrison, J. J., Bernath, P. F., and Kirchengast, G.: Spectroscopic requirements for ACCURATE, a microwave and infrared-laser occultation satellite mission, J. Quant. Spectrosc. Ra., 112, 2347–2354, 2011. 11615, 11616, 11624
- 20 Heimann, M.: Obituary: Charles David Keeling 1928–2005, Nature, 437, 331, doi:10.1038/437331a, 2005. 11596

Keeling, C. D.: Is carbon dioxide from fossil fuel changing man's environment?, P. Am. Philos. Soc., 114, 10–17, 1970. 11595

Kirchengast, G. and Schweitzer, S.: Climate benchmark profiling of greenhouse gases

- ²⁵ and thermodynamic structure and wind from space, Geophys. Res. Lett., 38, L13701, doi:10.1029/2011GL047617, 2011. 11596, 11609, 11616, 11617, 11622, 11624
 - Kirchengast, G., Bernath, P. F., Buehler, S., Durry, G., Facheris, L., Gerbig, C., Haimberger, L., Harris, J., Hauchecorne, A., Kurölä, E., Larsen, G. B., Sausen, R., Anthes, R. A., Gorbunov, M. E., Kursinski, E. R., Leroy, S. S., Trenberth, K., Randel, B., Gille, J., and Tsuda, T.:
- ACCURATE climate benchmark profiling of greeenhouse gases and thermodynamic variables and wind from space (ESA Earth Explorer Opportunity Mission EE-8 proposal), Sci. Rep. 36-2010, Wegener Center Verlag, Graz, Austria, available at: http://www.wegcenter.at/wcv (last access: 13 November 2014), 2010. 11596, 11597



- Kursinski, E. R., Syndergaard, S., Flittner, D., Feng, D., Hajj, G., Herman, B., Ward, D., and Yunck, T.: A microwave occultation observing system optimized to characterize atmospheric water, temperature and geopotential via absorption, J. Atmos. Ocean. Tech., 19, 1897–1914, doi:10.1175/1520-0426(2002)019019<1897:AMOOSO>2.0.CO;2, 2002. 11596
- 5 Messerschmidt, J., Chen, H., Deutscher, N. M., Gerbig, C., Grupe, P., Katrynski, K., Koch, F.-T., Lavrič, J. V., Notholt, J., Rödenbeck, C., Ruhe, W., Warneke, T., and Weinzierl, C.: Automated ground-based remote sensing measurements of greenhouse gases at the Białystok site in comparison with collocated in situ measurements and model data, Atmos. Chem. Phys., 12, 6741-6755, doi:10.5194/acp-12-6741-2012, 2012. 11596
- Proschek, V., Kirchengast, G., and Schweitzer, S.: Greenhouse gas profiling by infrared-10 laser and microwave occultation: retrieval algorithm and demonstration results from end-toend simulations, Atmos, Meas, Tech., 4, 2035–2058, doi:10.5194/amt-4-2035-2011, 2011, 11597, 11606, 11609, 11610

Proschek, V., Kirchengast, G., Emde, C., and Schweitzer, S.: Greenhouse gas profiling by

- infrared-laser and microwave occultation in cloudy air: results from end-to-end simulations, J. 15 Geophys. Res. Atmos., online first, doi:10.1002/2014JD021938, 2014. 11597
 - Rothman, L. S., Rinsland, C. P., Goldman, A., Massie, S. T., Edwards, D. P., Flaud, J.-M., Perrin, A., Camy-Peyret, C., Dana, V., Mandin, J.-Y., Schroeder, J., McCann, A., Gamache, R. R., Wattson, R. B., Yoshino, K., Cahnce, K. V., Jucks, K. W., Brown, L. R., Nemtchinov, V., and
- Varanasi, P.: The HITRAN molecular spectrosocopic database and HAWKS (Hitran Atmo-20 spheric WorKStation): 1996 edition, J. Quant. Spectrosc. Ra., 60, 665–710, 1998. 11615 Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., Boudon, V., Brown, L. R., Camparque, A., Champion, J.-P., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Fally, S., Flaud, J.-M., Gamache, R. R., Goldman, A., Jacquemart, D., Kleiner, I.,
- Lacome, N., Lafferty, W. J., Mandin, J.-Y., Massie, S. T., Mikhailenko, S. N., Miller, C. E., 25 Moazzen-Ahmadi, N., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V. I., Perrin, A., Predoi-Cross, A., Rinsland, C. P., Rotger, M., Šimečková, M., Smith, M. A. H., Sung, K., Tashkun, S. A., Tennyson, J., Toth, R. A., Vandaele, A. C., and Vander Auwera, J.: The HI-TRAN 2008 molecular spectroscopic database, J. Quant. Spectrosc. Ra., 110, 533-572,
- doi:10.1016/j.jgsrt.2009.02.013, 2009. 11604, 11614 30

Discussion Paper	AMTD 7, 11593–11652, 2014			
Iper Discussion Paper	valida greenhou for the Islands ex	Retrieval and validation of greenhouse gases for the Canary Islands experiment V. Proschek et al.		
per	Title	Title Page		
_	Abstract	Introduction		
Disc	Conclusions	References		
Discussion Paper	Tables	Figures		
Paper	14	۶I		
		•		
	Back	Close		
Discussion Pape	Full Screen / Esc			
n Pa	Printer-friendly Version			
aper	Interactive Discussion			



- Schweitzer, S.: The ACCURATE concept and the infrared laser occultation technique: mission design and assessment of retrieval performacne, Ph.D. thesis, Sci. Rep. 34-2010, Wegener Center Verlag, Graz, Austria, available at: http://www.wegcenter.at/wcv (last access: 13 November 2014), 2010. 11597, 11617
- Schweitzer, S., Kirchengast, G., and Proschek, V.: Atmospheric influences on infrared-laser signals used for occultation measurements between Low Earth Orbit satellites, Atmos. Meas. Tech., 4, 2273–2292, doi:10.5194/amt-4-2273-2011, 2011a. 11596, 11597, 11600, 11606, 11616

Schweitzer, S., Kirchengast, G., Schwärz, M., Fritzer, J. M., and Gorbunov, M. E.: Thermody-

- namic state retrieval from microwave occultation data and performance analysis based on end-to-end simulations, J. Geophys. Res., 116, D10301, doi:10.1029/2010JD014850, 2011b. 11597
 - Vadrevu, K. P. and Choi, Y.: Wavelet analysis of airborne CO₂ measurements and related meteorological parameters over heterogeneous landscapes, Atmos. Res., 102, 77–90, doi:10.1016/i.atmosres.2011.06.008. 2011. 11596
- WMO: Report of the 16th WMO/IAEA meeting of experts on carbon dioxide, other greenhouse gases, and related tracers measurement techniques (GGMT-2011), GAW Report No. 206, WMO TD No. 1553, Wellington, New Zealand, available at: http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_206_web.pdf (last access: 13 November 2014), 2012.
 11600, 11601

15

Wunch, D., Toon, G. C., Wennberg, P. O., Wofsy, S. C., Stephens, B. B., Fischer, M. L., Uchino, O., Abshire, J. B., Bernath, P., Biraud, S. C., Blavier, J.-F. L., Boone, C., Bowman, K. P., Browell, E. V., Campos, T., Connor, B. J., Daube, B. C., Deutscher, N. M., Diao, M., Elkins, J. W., Gerbig, C., Gottlieb, E., Griffith, D. W. T., Hurst, D. F., Jiménez, R., Keppel-Aleks, G., Kort, E. A., Macatangay, R., Machida, T., Matsueda, H., Moore, F., Morino, I., Park, S., Robinson, J., Roehl, C. M., Sawa, Y., Sherlock, V., Sweeney, C., Tanaka, T., and Zondlo, M. A.: Calibration of the Total Carbon Column Observing Network using aircraft profile data, Atmos. Meas. Tech., 3, 1351–1362, doi:10.5194/amt-3-1351-2010, 2010. 11596
Yang, Z., Toon, G. C., Margolis, J. S., and Wennberg, P. O.: Atmospheric CO₂ retrieved from ground-based near IR solar spectra, Geophys. Res. Lett., 29, 53-1–53-4, doi:10.1029/2001GL014537. 2002. 11596





Yokota, T., Yoshida, Y., Eguchi, N., Ota, Y., Tanaka, T., Watanabe, H., and Maksyutov, S.: Global concentrations of CO₂ and CH₄ retrieved from GOSAT: first preliminary results, SOLA, 5, 160-163, 2009. 11596

Yoshida, Y., Ota, Y., Eguchi, N., Kikuchi, N., Nobuta, K., Tran, H., Morino, I., and Yokota, T.:

Retrieval algorithm for CO₂ and CH₄ column abundances from short-wavelength infrared 5 spectral observations by the Greenhouse gases observing satellite, Atmos. Meas. Tech., 4, 717-734, doi:10.5194/amt-4-717-2011, 2011. 11596

AMTD 7, 11593–11652, 2014					
Retrieval and validation of greenhouse gases for the Canary Islands experiment					
	Page Introduction				
Conclusions Tables	References Figures				
Printer-frier	Close cen / Esc dly Version Discussion				
	7, 11593–1 Retriev valida greenhou for the Islands ex V. Prosc Title Abstract Conclusions Tables I Back Full Scree Printer-frier				



Table 1. GPS-derived positions of the telescopes/parking lot and the validation stations at the transmitter (Tx) and receiver (Rx) sites. The meteorological station nearby the OGS is named GONG (its customary local name) and the Cavity ring-down spectrometer for in situ GHG measurements of the company Picarro is named CRDS. Table 3 provides more details on the datasets themselves.

Site	Name	Latitude [deg]	Longitude [deg]	Altitude [m]
Тх	NOT parking lot NOT meteo station CRDS Picarro	28.75720 28.75690 28.75660	-17.88502 -17.88498 -17.88505	2390 2398 2390
Rx	OGS telescope GONG meteo station CRDS Piccarro Sampling flasks	28.30097 28.30058 28.30103 28.30103	-16.51183 -16.51218 -16.51192 -16.51192	2393 2393 2393 2393 2393





Table 2. Pre-processed infrared-laser link datasets available for the GHG retrieval. For description see Sect. 2.1.

File	Date	Laser	No. of	Wave	number ran	•	Time range			
No.		ID	spectra	V _{Start}	VEnd	Δv	t _{Start}	t _{End}	Δt	
	[dd/mm]				[cm ⁻¹]		[hh:m	im:ss]	[mm:ss]	
F1	21 Jul	L2	14	4768.03	4768.92	0.89	01:50:07	01:55:06	04:59	
F2	21 Jul	L1	22	4770.99	4774.49	3.50	02:22:51	02:29:58	07:07	
		L2	25	4766.37	4768.16	1.79	02:22:42	02:30:07	07:25	
F3	21 Jul	L1	23	4770.98	4774.52	3.54	02:31:18	02:38:46	07:28	
		L2	24	4766.37	4768.17	1.80	02:31:09	02:38:37	07:28	
F4	21 Jul	L1	7	4770.99	4774.54	3.55	02:40:52	02:43:04	02:12	
		L2	8	4766.36	4768.19	1.83	02:40:43	02:43:12	02:29	
F5	21 Jul	L1	48	4768.45	4769.34	0.89	03:27:09	03:41:49	14:40	
F6	21 Jul	L1	92	4768.24	4771.86	3.62	04:32:03	05:04:08	32:05	
		L2	73	4763.95	4768.21	4.26	04:32:14	05:03:59	31:45	
F7	21 Jul	L2	32	4768.56	4769.49	0.93	22:15:04	22:29:15	14:11	
F8	21 Jul	L2	19	4768.57	4769.50	0.93	22:36:54	22:43:34	06:40	
F9	21 Jul	L1	5	4770.34	4771.20	0.86	22:59:03	23:00:10	01:07	
		L2	3	4768.48	4769.42	0.94	22:59:28	23:00:02	00:36	
F10	21 Jul	L1	49	4770.36	4771.20	0.84	23:19:57	23:34:52	14:55	
		L2	38	4768.48	4769.44	0.96	23:20:06	23:34:42	14:36	
F11	22 Jul	L1	38	4768.27	4771.75	3.48	00:14:34	00:33:05	18:31	
		L2	36	4763.99	4767.97	3.98	00:14:19	00:32:54	18:35	
F12	22 Jul	L1	17	4768.19	4771.79	3.60	00:33:53	00:42:53	09:00	
		L2	19	4764.11	4768.15	4.04	00:34:04	00:43:04	09:00	
F13	22 Jul	L1	48	4770.92	4774.52	3.60	00:54:17	01:12:47	18:30	
		L2	37	4766.36	4768.19	1.83	00:54:28	01:12:36	18:08	
F14	22 Jul	L1	10	4770.92	4774.54	3.62	01:14:28	01:17:59	03:31	
		L2	8	4766.37	4768.19	1.82	01:14:42	01:17:45	03:03	
F15	22 Jul	L1	18	4773.81	4777.55	3.74	01:31:29	01:37:50	06:21	
		L2	14	4766.36	4768.19	1.83	01:31:40	01:38:01	06:21	
F16	22 Jul	L1	34	4773.83	4777.59	3.76	01:56:06	02:08:53	12:47	
		L2	25	4766.37	4768.20	1.83	01:56:17	02:08:42	12:25	
F17	22 Jul	L2	34	4768.68	4769.60	0.92	02:55:54	03:09:07	13:13	
F18	22 Jul	L3	28	4346.50	4347.45	1.95	05:44:42	05:51:25	06:43	
F19	22 Jul	L3	47	4345.94	4348.83	2.89	06:21:09	06:37:49	16:40	

AMTD 7, 11593–11652, 2014 **Retrieval and** validation of greenhouse gases for the Canary **Islands experiment** V. Proschek et al. Title Page Introduction Abstract Conclusions References Tables Figures Back Close Full Screen / Esc Printer-friendly Version Interactive Discussion

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper



	AMTD 7, 11593–11652, 2014					
Retrieval and validation of greenhouse gases for the Canary Islands experiment V. Proschek et al.						
Title	Title Page					
Abstract	Introduction					
Conclusions	References					
Tables	Figures					
14	►I					
•	•					
Back	Close					
Full Scr	Full Screen / Esc					
Printer-frie	Printer-friendly Version					
Interactive Discussion						

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

CC D

Table 3. Validation dataset taken, or used from available sources, during the measurement campaign. For description see Sect. 2.2.

	Tx (NOT)	Rx (OGS)	Notes
Meteo data	NOT station p, T, RH, V	GONG station p, T, RH, V	continuous measurements
CRDS Piccarro	CO ₂ , H ₂ O, CH ₄ ,	CO_2 , H_2O , CH_4 ,	continuous measurements by MPI-BGC, time resolution 2.5 s, precision better than 0.1 ppm 1 ppb, and 5 % for CO_2 , CH_4 and H_2O , respectively
Sampling flasks	-	¹² CO ₂ , ¹³ CO ₂ , C ¹⁸ OO, CH ₄	analysis performed at MPI-BGC, measurement during IR signal receiving phase
ECMWF data	interpolated valu	ue at Tx, Rx, along ray path p, T, H_2O	six-hourly analysis, grid resolution of ~ 14 km (T1279), 91 height levels, four UTC layers per day

Table 4. Absorption line center frequencies and corresponding reference frequency allocations used in the retrieval, complemented by information on spectroscopic parameter uncertainties from HITRAN08 for the two most relevant line parameters, line intensity and air-broadened halfwidth.

Species peak ID	Abs. line [cm ⁻¹]	Ref. line [cm ⁻¹]	Δ(Abs-Ref) [cm ⁻¹]	ΔS [%]	$\Delta \gamma_{air}$ [%]
·				[/0]	[/0]
¹² CO ₂ -1	4767.37	4767.20	0.17	\geq 10 and < 20	\geq 5 and < 10
¹² CO ₂ -2	4772.63	4772.82	-0.19	\geq 10 and < 20	≥ 5 and < 10
¹³ CO ₂ -1	4766.64	4766.40	0.24	\geq 10 and < 20	\geq 5 and < 10
C ¹⁸ OO-1	4767.04	4767.20	-0.16	\geq 10 and < 20	\geq 5 and < 10
C ¹⁸ OO-2	4768.79	4768.90	0.11	\geq 10 and < 20	≥ 5 and < 10
C ¹⁸ OO-3	4770.53	4770.20	0.33	\geq 10 and < 20	\geq 5 and < 10
H ₂ O-1	4768.40	4768.68	-0.28	≥ 5 and < 10	< 1
H ₂ O-2	4776.59	4776.75	-0.16	≥ 5 and < 10	\geq 1 and < 2
CH ₄ -1	4346.73	4346.95	-0.22	≥ 2 and < 5	<u>≥</u> 20
CH ₄ -2	4348.16	4348.33	-0.17	\geq 2 and < 5	\geq 2 and < 5





Table 5. Spectral correction terms ΔT_{SC} estimated for the ten chosen GHG absorption lines of the nineteen IR-laserlink data files available for retrieval processing. An uncertainty of ±0.1 dB was co-estimated for the ΔT_{SC} best-estimate values of 0.79, 0.59 and 0.53, of ±0.09 dB for 0.49, of ±0.08 dB for 0.33 and 0.23, and of ±0.07 dB for 0.13, respectively. The CH₄ ΔT_{SC} values were estimated as 1.6 and 0.6, with an uncertainty of ±0.13 dB. The numbers in bold represent the measurements with laser L1 and the upright numbers those with laser L2; the CH₄ measurements were performed with laser L3.

File										
No.	¹³ CO ₂ -1	C ¹⁸ OO-1	¹² CO ₂ -1	H ₂ O-1	C ¹⁸ OO-2	C ¹⁸ OO-3	¹² CO ₂ -2	H ₂ O-2	CH ₄ -1	CH ₄ -2
F1	х	х	х	0.59	х	х	х	х	х	х
F2	0.79	0.33	0.53	х	х	х	0.59	х	х	х
F3	0.79	0.33	0.53	х	х	х	0.59	х	х	х
F4	0.79	0.33	0.53	х	х	х	0.59	х	х	х
F5	х	х	х	х	0.33	х	х	х	х	х
F6	0.49	0.13	0.23	0.59	0.33	0.13	х	х	х	х
F7	х	х	х	х	0.23	х	х	х	х	х
F8	х	х	х	х	0.23	х	х	х	х	х
F9	х	х	х	х	0.23	0.33	х	х	х	х
F10	х	х	х	х	0.23	0.33	х	х	х	х
F11	0.59	0.23	0.33	0.59	0.33	0.13	х	х	х	х
F12	0.59	0.23	0.33	0.59	0.33	0.13	х	х	х	х
F13	0.79	0.33	0.53	х	х	х	0.59	х	х	х
F14	0.79	0.33	0.53	х	х	х	0.59	х	х	х
F15	0.79	0.33	0.53	х	х	х	х	0.33	х	х
F16	0.79	0.33	0.53	х	х	х	х	0.33	х	х
F17	х	х	х	х	х	х	х	х	х	х
F18	х	х	х	х	х	х	х	х	1.6	х
F19	х	х	х	х	х	х	х	х	х	0.6

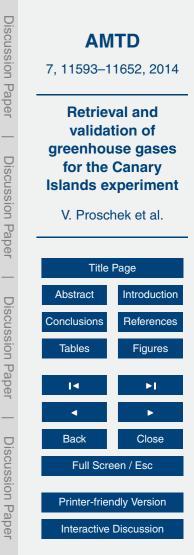




Table 6. Estimated uncertainties $\Delta \mathcal{V}$ in retrieved GHG volume mixing ratios \mathcal{V} , for the ten selected species absorption lines. The estimates include uncertainties in \mathcal{V} due to spectral-correction-term uncertainty, spectroscopic uncertainty, water vapor uncertainty, and pressure and temperature uncertainty. The resulting combined uncertainty is shown as well.

Species peak ID	$\Delta \mathcal{T}_{SC}$ Uncert. ± $\Delta \mathcal{V}$ [%]	Spectr. Uncert. ±ΔV [%]	H_2O Uncert. ± $\Delta \mathcal{V}$ [%]	p, T Uncert. ± $\Delta \mathcal{V}$ [%]	Combined Uncert. $\pm \Delta \mathcal{V} [\%]$
¹² CO ₂ -1	4.6	10	2.3	6.0	12.7
¹² CO ₂ -2	4.4	10	0.5	6.0	12.5
¹³ CO ₂ -1	4.5	10	1.5	0.5	11.1
C ¹⁸ OO-1	8.2	10	6.0	1.0	14.3
C ¹⁸ OO-2	7.6	10	4.0	1.0	13.2
C ¹⁸ OO-3	6.5	10	0.5	1.0	12.0
H ₂ O-1	4	8	50	3.5	50.9
H ₂ O-2	2	8	50	3.5	50.8
CH ₄ -1	8.4	20	4.3	1.0	22.1
CH ₄ -2	8.3	5	0.3	1.0	9.7



Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper



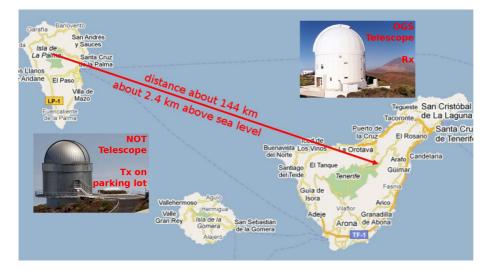
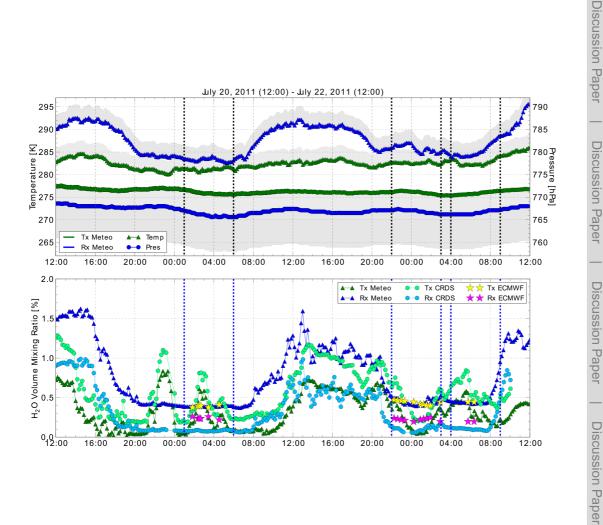
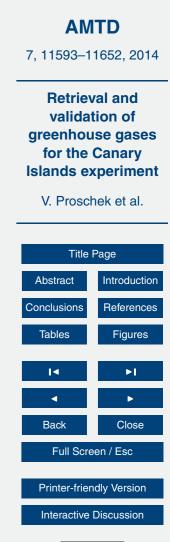


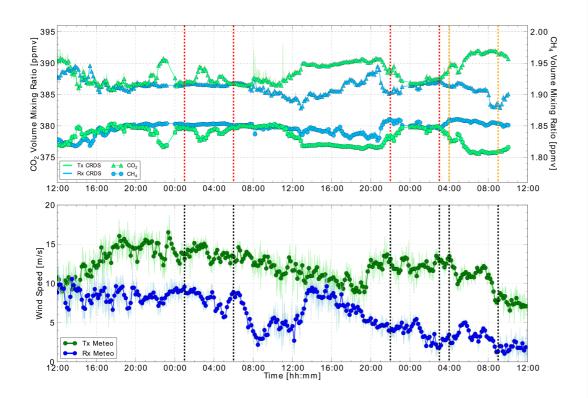
Figure 1. Schematic view of the ~ 144 km long-range infrared-laser link between La Palma (Tx) and Tenerife (Rx) and illustrative pictures of the NOT parking lot location and the OGS telescope.











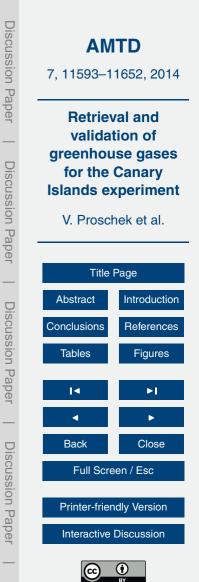


Figure 2. Time series of meteorological weather data and GHG validation data spanning over the infrared-laser link measurements periods, which are delimited by dotted vertical lines (cf. times in Table 2). Top panel: 10 min-averaged temperature (triangles) and pressure (circles) data from the weather stations at the Tx (green) and Rx (blue) sites; the gray-shaded areas indicate the respective deviations of the co-located ECMWF data at the Tx and Rx sites. Uppermiddle panel: 10 min-averaged H₂O volume mixing ratio (\mathcal{V}) from the meteorological weather stations (triangles), the CRDS instruments (circles), and co-located ECMWF data (stars; those interpolated to infrared-laser link measurement times) at the Tx and Rx sites. Lower-middle panel: 10 min-averaged CRDS \mathcal{V} data for CO₂ (triangles) and CH₄ (circles) at the Tx and Rx sites. Bottom panel: 10 min-averaged wind speed (circles), and underlying 1 min values (light-colored fluctuating time series), from the weather stations at the Tx (green) and Rx (blue) sites.



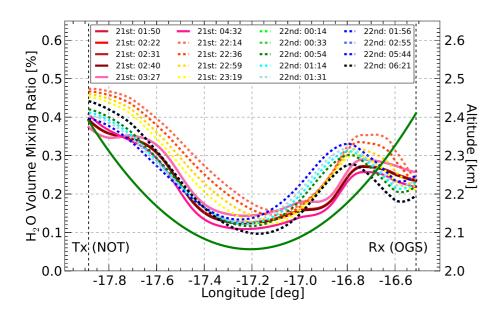
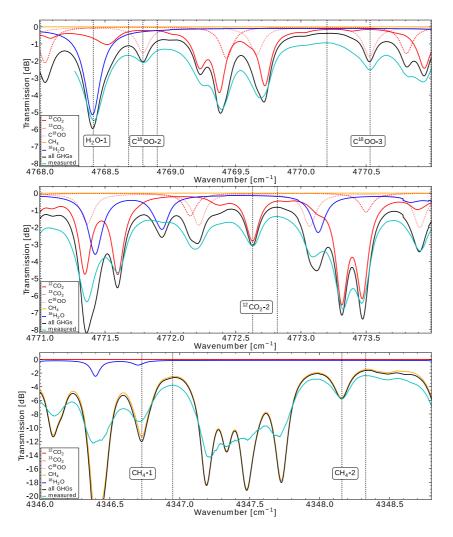


Figure 3. H_2O volume mixing ratio along the Tx-to-Rx ray path (longitude coordinate shown) based on interpolated ECMWF analysis fields, for ray-tracing performed at the starting time of each IR-laser link data file (Table 2). In addition, the altitude of the ray path above mean-sealevel is indicated (heavy green line; right-hand-side axis), which, due to Earth's curvature over the 144 km distance, is more than 300 m lower at mid-distance than the altitudes of the Tx and Rx sites.





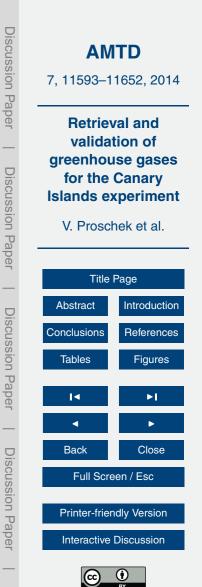


Figure 4. Examples of simulated transmission spectra of targeted GHG isotopes (see in-panel legends; for H_2O and CH_4 the main isotopes are utilized), of corresponding total transmission spectra from all GHGs (black curves), and of associated measured spectra (cyan curves). The respective absorption line center frequencies and nearby reference frequencies, according to Table 4, are marked by dash-dotted vertical lines and the corresponding target GHGs are noted below the respective absorption line peaks. Three example wavenumber ranges are illustrated, one containing lines for H_2O-1 , $C^{18}OO-2$, and $C^{18}OO-3$ (top panel), one for ${}^{12}CO_2$ (middle panel), and one for the two lines chosen for CH_4 (bottom panel).





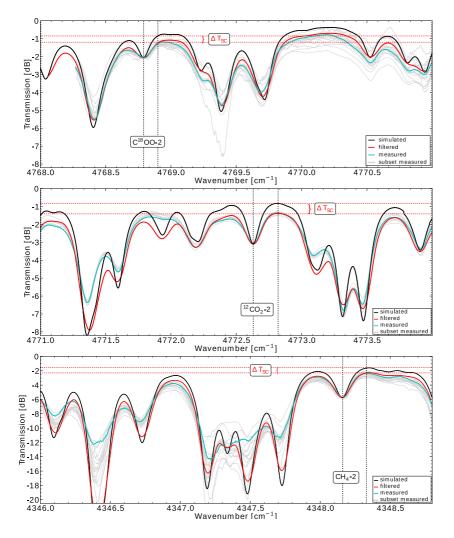
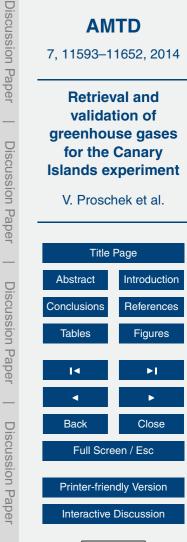




Figure 5. Examples of simulated spectra (black), filtered simulated spectra (red), and measured spectra (cyan) from a typical set of measured spectra (gray), illustrating spectral broadening of target GHG absorption lines in the measured spectra and the approach of correcting for the associated differential transmission error between absorption and reference channels. The wavenumber ranges illustrated in the three panels are the same as in Fig. 4 and the absorption lines illustrating the spectral broadening correction are marked in the same way as in Fig. 4. $\Delta \mathcal{T}_{SC}$ marks the increment of differential transmission that is missing due to the line broadening in the measured data and that is therefore to be corrected for. The bundle of measured spectra shown in gray illustrates that any correction term $\Delta \mathcal{T}_{SC}$ will also bring in some added uncertainty.



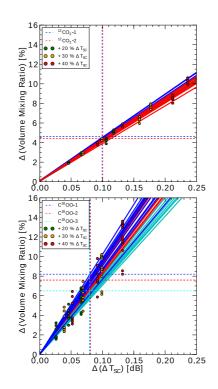


Figure 6. Examples for the linear dependence of volume mixing ratio uncertainty $\Delta(\mathcal{V})$ (%) on spectral correction term uncertainty $\Delta(\Delta \mathcal{T}_{SC})$ (dB), for the ${}^{12}CO_2$ -1|2 peaks (upper panel; blue and red) and the C¹⁸OO-1|2|3 peaks (lower panel; blue, red, cyan). The linear transfer functions (bundles of colored solid lines per species peak), and the cross-check results for the $\Delta(\mathcal{V})[\Delta(\Delta \mathcal{T}_{SC})]$ relation from actual retrieval (color-filled circles), are explained and discussed in Sect. 4.1.





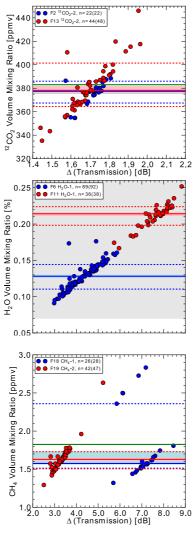




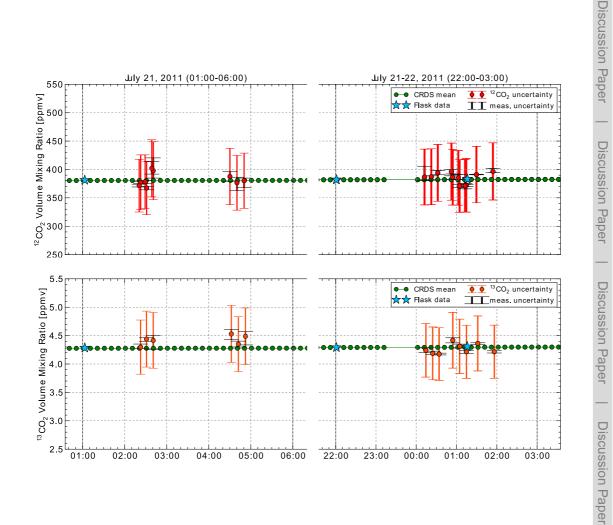


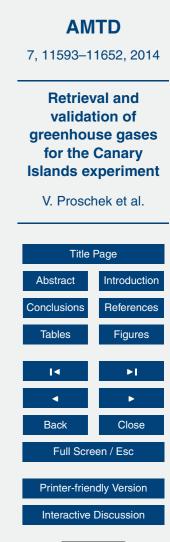


Figure 7. Examples of retrieved ensembles of volume mixing ratios within ~ 10 min periods, for absorption lines of ¹²CO₂ (top panel, data from files F2 and F13), H₂O (middle panel, data from files F6 and F11), and CH₄ (bottom panel, data from files F18 and F19), as function of the measured ΔT (Eq. 1). Individual retrievals are shown (color-filled circles, one red and one blue example ensemble per panel) together with markers (horizontal lines and shaded areas) of: the Tx/Rx-averaged CRDS reference value (green line, except for H₂O), the CRDS reference data uncertainty range (gray-shaded area, almost covering the H₂O panel and almost invisibly small for ¹²CO₂ and CH₄), the median value of the retrievals (red/blue solid lines, partially overlapping), the "± σ/\sqrt{n} " range of the retrievals (light red/light blue-shaded areas, partially overlapping). The number of individual retrievals per ensemble (*n*) is indicated in the legend both after the outlier rejection and before the outlier rejection (the latter shown as value in parentheses).









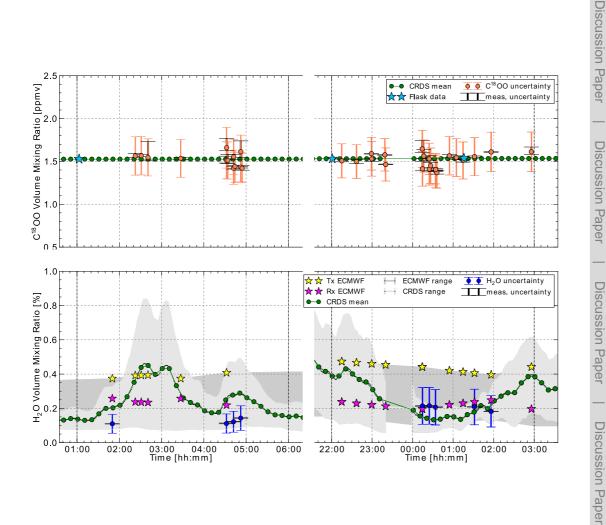






Figure 8. Retrieval results for ¹²CO₂ (top panel), ¹³CO₂ (upper-middle panel), C¹⁸OO (lower-middle panel), and H₂O (bottom panel) volume mixing ratios for the ~ 10 min periods of all available species data from the two successful campaign nights of 21 July 2011 (within 01:00 to 06:00 UTC) and 21–22 July 2011 (within 22:00 to 03:00 UTC). For each available ~ 10 min period of a retrieved species, the average value (median; red/blue-filled circle), the estimated combined uncertainty (red/blue "error bar"), and the statistical uncertainty of the average (black "error bar", generally overlapped by the red/blue "error bar" and of much smaller range) are shown. For validation reference, the 10 min-averaged CRDS reference data (green-filled circles), the flask CO₂ data (blue-colored stars in upper three panels), and the Tx/Rx-collocated ECMWF H₂O data (yellow/magenta-colored stars in bottom panel) are shown. For H₂O (bottom panel), also the uncertainty ranges of the CRDS data (light gray-shaded area) and ECMWF data (gray-shaded area) are indicated.



