Comment on acp-2021-307

Anonymous Referee #2

Referee comment on "Twenty years of ground-based NDACC FTIR spectrometry at Izaña Observatory – overview and long-term comparison to other techniques" by Omaira E. García et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-307-RC3, 2021

Response to Referee#2

The authors would like to thank the Referee for reviewing carefully this paper and provide valuable and constructive comments that have improved this work. In the following text, the Referee suggestions (in blue italics) are addressed in detail (the authors' responses are in plain text).

General comment

Manuscript by Omaira E. García et al. titled "Twenty years of ground-based NDACC FTIR spectrometry at Izaña Observatory - overview and long-term comparison to other techniques" presents a comprehensive analysis of the long-term FTIR-monitoring which is being carried out at Izaña Observatory. Izaña Observatory whose history dates back to 1916, has a strategic location for the investigation of atmospheric processes and contributes to numerous international programmes and observational networks (GAWWMO, WDCGG, WOUDC, NDACC, TCCON, AERONET, BSRN, MPLNET, E-GVAP, NOAA/ESRL/GMD CCGG, etc.).

Authors provided a thorough description of the unique FTIR-experiment which was started in 1999. The abstract clearly presents the subject matter and findings of the paper. The scientific basis of the results reported in the paper is the reliable and recognized technique of atmospheric FTIR-spectrometry, and widely used inverse methods for atmospheric sounding (formalism by Rodgers(2000)). Both, the acquisition of MIR spectra of direct solar radiation using FTIR-system installed at Izaña Observatory and the following FTIRspectra processing are described by authors in detail.

The investigated time series of C2H6, CH4, ClONO2, CO, HCl, HCN, H2CO, HF, HNO3, N2O, NO2, NO, O3, OCS, and three isotopologues of water vapour (H216O, H218O, and HDO) are of fundamental importance to the atmospheric studies including the interactions of atmospheric composition and climate, the investigation of trace gases temporal variations and processes driven these variations, the verification of modern CTMs (chemical transport models) and the validation of satellite observations. The manuscript is well-written and structured, contains new results that can be of interest to scientific community. Bibliography, in general, provides a relevant list of references, nevertheless, according to referee's opinion, the number of references could be reduced because the bibliography section occupies about one six of the whole paper volume.

The authors agree with the Referee in that the number of references is excessive, therefore they will be revised and reduced accordingly in the revised manuscript.

Specific comments

1) Lines 131-134: "By evaluating spectral signatures of vibrational-rotational transitions contained in the solar absorption spectra measured, the FTIR technique allows total column amounts and low-resolution vertical profiles of different atmospheric trace gases to be retrieved with a high degree of precision." The "degree of precision" is expected to be different for different trace gases and not necessarily "high" for those retrieved species which have weak absorption signatures in the analyzed FTIR-spectra. If statistical errors/uncertainties can be considered as a measure of "degree of precision", we can see in Table 3 that these errors can reach ~50% for H2CO and ~100% for ClONO2.

As stated by the Referee, the FTIR technique provides high-quality observations for many trace gases, but its quality indeed depends on the target gas. To avoid confusions, the statement "with a high degree of precision" will be removed in the description of the FTIR technique in the Introduction section.

2) Section 3.1: Whether FTIR-instruments (an IFS 120M and an IFS 120/5HR) at Izaña Observatory have been operated remotely or by an operator/technician? Could you please specify?

The IFS 120M instrument (1999-2005) was operated manually by a technician between 1999-2005, while the IFS 120/5HR was also operated manually until 2012 when the instrument was adapted to be controlled remotely. Although this instrument works remotely, it is not an automatic system (i.e. a technician has to run the whole system, albeit not necessarily on site). This information will be added to Section 3.1. and Table 1.

3) Lines 209-211: "The only quality filter applied on public FTIR products is that observations taken at high solar zenith angles (≥85°) have been excluded to avoid imprecise retrievals (mainly caused by misalignments of the solar tracker or spectroscopic issues). These data represent less than 1% of the total data set." It is expected that clouds are one of the most important factor leading to the outliers in retrieval results. Are the FTIR-observations at Izaña Observatory free of this effect?

At Izaña Observatory (IZO) the FTIR spectra are only recorded when the line of sight between the instrument and sun is cloud free. Note that, as mentioned above, the FTIR system at IZO is not an automatic system, so the operator decides when the instrument takes measurements. However, to avoid possible contamination of thin clouds, the FTIR observations are, in a second step, filtered according to coincident global solar radiation observations taken at IZO in the framework of the Baseline Solar Radiation Network (BSRN, http://bsrn.awi.de). By using a cloud detection method on the coincident solar radiation measurements (based on Long and Ackerman, 2000, and adapted for IZO by García et al., 2014a), the cloud-free periods in the FTIR records are easily identified. Finally, during the operational analysis, unstable or imprecise FTIR retrievals usually lead to non-convergence of the inversion procedure, which is likely due to remaining thin clouds or other local factors.

4) Lines 191-193: "Most relevant changes are those related to CH4, for which the spectral micro-windows are adopted from Sepúlveda et al. (2014), and the spectroscopy parameters correspond to the improved linelist provided by Dubravica et al. (2013)." What are the principle differences between CH4 retrieval strategies reported in Sepúlveda et al. (2014) and Sussmann et al. (2011)? Does the modified CH4 retrieval strategy by Sepúlveda et al. (2014) provide the *homogeneous results with other IRWG-NDACC sites which make retrievals according to Sussmann et al. (2011)? Please, clarify this.*

Reference: Sussmann, R., Forster, F., Rettinger, M., and Jones, N.: Strategy for highaccuracy-and-precision retrieval of atmospheric methane from the mid-infrared FTIR network, Atmos. Meas. Tech., 4, 1943–1964, https://doi.org/10.5194/amt-4-1943-2011, 2011.

The methane (CH_4) retrieval strategy used at IZO, described in detail in Sepúlveda et al. (2014), is essentially the same as the one described in Sepúlveda et al. (2012), where the CH_4 profile retrievals from mid-infrared FTIR spectra were presented for the relatively-dry high-mountain site of Izaña. Sepúlveda et al. (2014) further broadened that work by proving that this retrieval strategy could be successfully applied on different NDACC sites covering different environments (altitude, latitude, and humidity).

The main differences between the Sepúlveda and Sussmann approaches are related to the spectral micro-windows selected, the methane spectroscopic linelist used, and the treatment of water vapour, as summarised in Table 1 below.

The Sussmann strategy (so-called MIR-GBM v1.0 in Sussmann et al., 2011) uses the 2000 version of HITRAN database (including the 2001 update release), three spectral micro windows between 2613-2922 cm^{-1} (see Table 1), and the water vapour profiles, which are scaled from a climatological profile. As stated in Sussmann et al. (2011), the MIR-GBM v1.0 is the optimum of 24 tested retrieval strategies, covering different spectral micro-window selections and HITRAN version (2000, 2004 and 2008), as it provides the best performance according to the absolute H_2O/HDO-CH_4 interference error. Note that dominant errors of the non-optimum retrieval strategies were found to be the systematic H_2O/HDO-CH_4 interference errors leading to a seasonal bias of up to ≈5%.

CH_4 Retrieval Strategy	Sussmann et al. (2011)	Sepúlveda et al. (2014)
Micro-windows [cm^{-1}]	2613.70–2615.40 2835.50–2835.80 2921.00– 2921.60	2611.60-2613.35 2613.70-2615.40 2835.55-2835.80 2903.82-2903.925 2914.70-2915.15 2941.51-2942.22
Spectroscopic database	HITRAN 2000 including 2001 update release	HITRAN 2008 including 2009 update release for H_2O, and Dubravica et al. (2013) update for CH_4
Water vapour treatment	Scale of climatological profiles	Simultaneous H_2O and HDO profile retrieval

Table 1. Main differences between the CH_4 retrieval strategies presented in Sussmann et al. (2011) and Sepúlveda et al. (2014).

On the other hand, the Sepúlveda work proposes six micro-windows (see Table 1 below), which contain strong, not saturated, and well-isolated CH_4 absorption lines as well as H_2O and HDO lines, in order to better account for the H_2O and HDO interferences. The H_2O and HDO profiles are simultaneously retrieved with CH_4 using a dedicated profiling retrieval. This approach seeks to minimise the impact of water vapour interferences, which might play a key role for humid low-altitude sites, as documented in Sussmann et al. (2011). Finally, the Sepúlveda strategy uses the HITRAN 2008 spectroscopy database for the forward simulations (with 2009 updates, Rothman et al., 2009), except for the target species CH_4, for which they use the improved CH_4 line parameters presented in Dubravica et al. (2013). The latter was found to provide lower spectroscopic residuals than the HITRAN 2008 linelist.

As discussed in detail in Hase et al. (2011), the Sepúlveda method generates CH_4 columns in agreement with the Sussman approach for different humidity conditions (subtropical high-mountain Izaña, mid-latitude Karlsruhe, and polar Kiruna sites). However, Hase et al. (2011) also documented that the Sepulveda strategy could be less dependent on humidity conditions as it minimises perturbing H_2O/HDO absorptions and it handles the problematic interference species H2O/HDO in a rigorous manner. Additionally, Sepúlveda et al. (2012) showed that their approach proved advantageous for reproducing the in-situ annual cycle and yearly mean time series when tropospheric FTIR products were compared to in-situ CH_4 records acquired in the framework of GAW-WMO programme at IZO. The difference is presumed to be due to different treatment of water vapour and the use of different line lists for CH_4.

This explanation will be introduced briefly in Section 3.3 of the revised manuscript.

5) Fig.14 (page 37) and Fig.15 (page 41): This is not easy to distinguish between the sizes of dots which correspond to R2=0.5 and R2=0.3.

The area of dots in Figure 14 and 15 will be modified to make them easier to evaluate.

6) Maybe, it is worth adding to manuscript a table summarizing all the long-term trends reported and discussed in the text in Sections 5, 6, and 8. Such a table will simplify reading and navigation through the manuscript.

According to the Referee's suggestion, a new table summarising the trend values discussed in the text will be added to the revised manuscript.

7) Section 5, Fig.7, and Appendix B: Which methods and/or criteria were implemented for the selection of an optimal set of frequencies used for the construction of multi-regression fit presented in Fig.7? Evaluation of statistical significance, cross-validation, etc.?

On the one hand, the multi-regression model used accounts for the intra-annual variation (season cycle), for which frequencies up to $2yr^{-1}$ (P=2) have been selected. Numerous works in the literature have proved that seasonal cycle variations can be properly described with this number of frequencies for many trace gases. See, for example, CH_4 (Gardiner et al., 2008; Sepúlveda et al., 2012, 2014; García et al., 2018), CO (Gardiner et al., 2008), HCHO (Vigoroux et al., 2018), N_2O (Gardiner et al., 2008; García et al., 2014b), NO_2 (Yela et al., 2017), OCS (Hannigan et al., 2021), and O_3 (Gardiner et al. 2008; García et al., 2012; Vigouroux et al., 2015).

On the other hand, the inter-annual variations are modelled with a Fourier series that considers all frequencies between 1 and N – 1, where N is the total number of years covered by the whole time series (Sepúlveda et al., 2014). This selection ensures that the fitted curve is able to adapt to relatively fast changes of the measured time series and waves such as those induced by dynamical variations of atmospheric transport circulation (see, for example, the NO, HNO_3 or OCS time series in Figure 7 of the preprint).

To ensure that the multi-regression model used properly captures the evolution of measured FTIR observations at the different timescales, the normality of the residuals (differences between the measured data series and the modelled one) was analysed. To do so, the one-sample Kolmogorov-Smirnov test (Kolmogorov, 1933; Smirnov, 1948) was applied to all residual time series, confirming residuals are normally distributed for all the trace gas analysed.

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