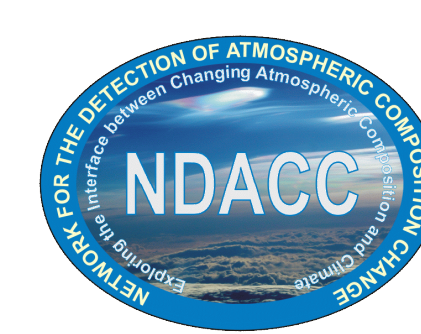
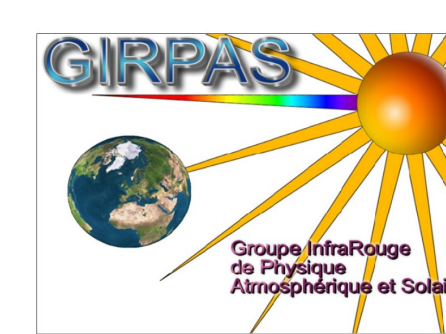


First retrievals of methanol (CH₃OH) above Jungfrauoch (46.5°N) : Optimization of retrieval strategy and information content.

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Instrumentation, Site and Observational Database

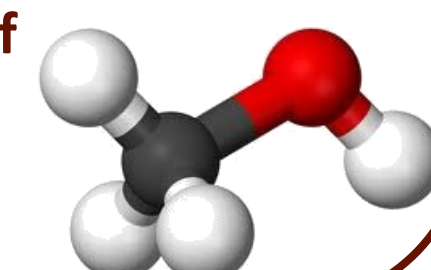
Our observational database is composed of recordings from two high resolution Fourier Transform InfraRed (FTIR) spectrometers (namely a homemade and a Bruker IFS-120HR) operated under clear sky conditions at the International Scientific Station of the Jungfrauoch (46.5°N, 8°E, 3580 m a.s.l.) since the early 1990s. This site is located in the Swiss Alps on the saddle between the Jungfrau (4158 m) and the Mönch (4107 m) summits.

The IR solar absorption monitoring is into regular operation since 1984. Since 1991, the FTIR instrument is affiliated to the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, visit <http://www.ndacc.org>). Both spectrometers are equipped with HgCdTe and InSb cooled detectors allowing us to cover the 650 to 4500 cm⁻¹ region of the electromagnetic spectrum. All high resolution (0.004 and 0.006 cm⁻¹) spectra investigated here have been recorded in 2010 with a Bruker IFS-120HR instrument and range from 700 to 1400 cm⁻¹.

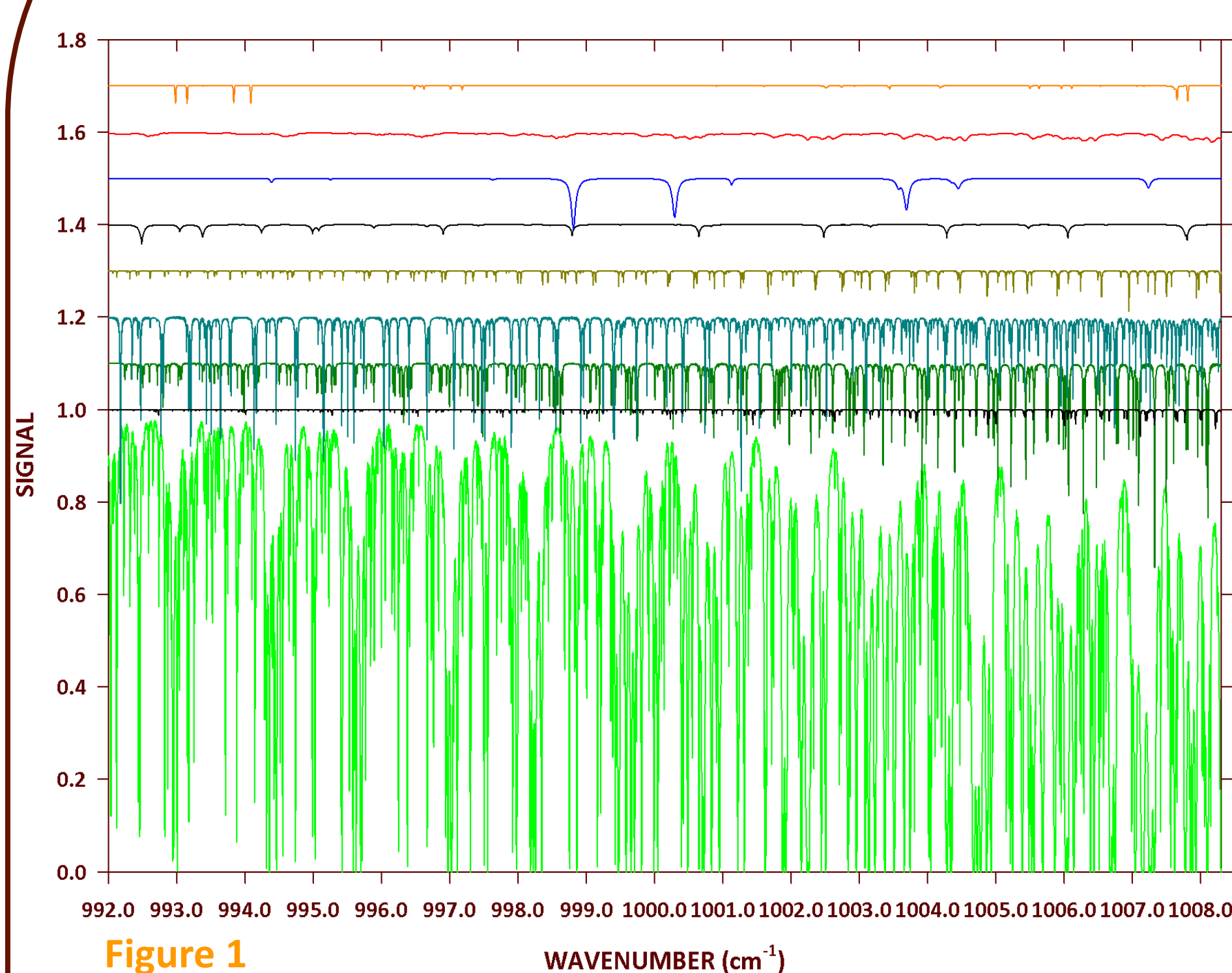


Methanol

- Methanol (CH₃OH) is an organic compound of the atmosphere with concentrations close to a few ppbv. Despite a lifetime of a few days (Jacob *et al.*, 2005) CH₃OH is the second most abundant organic molecule in the atmosphere (after methane).
- Natural sources of CH₃OH include plant growth, oceans, decomposition of plant matter, oxidation of methane and other VOCs,...
- Anthropogenic sources are from vehicles, industry, biomass burning completes the emission budget.
- The main sink is the oxidation by hydroxyl radical, leading to the formation of carbon monoxide (CO) and formaldehyde (H₂CO).



-A- Microwindows - Limits and interfering species



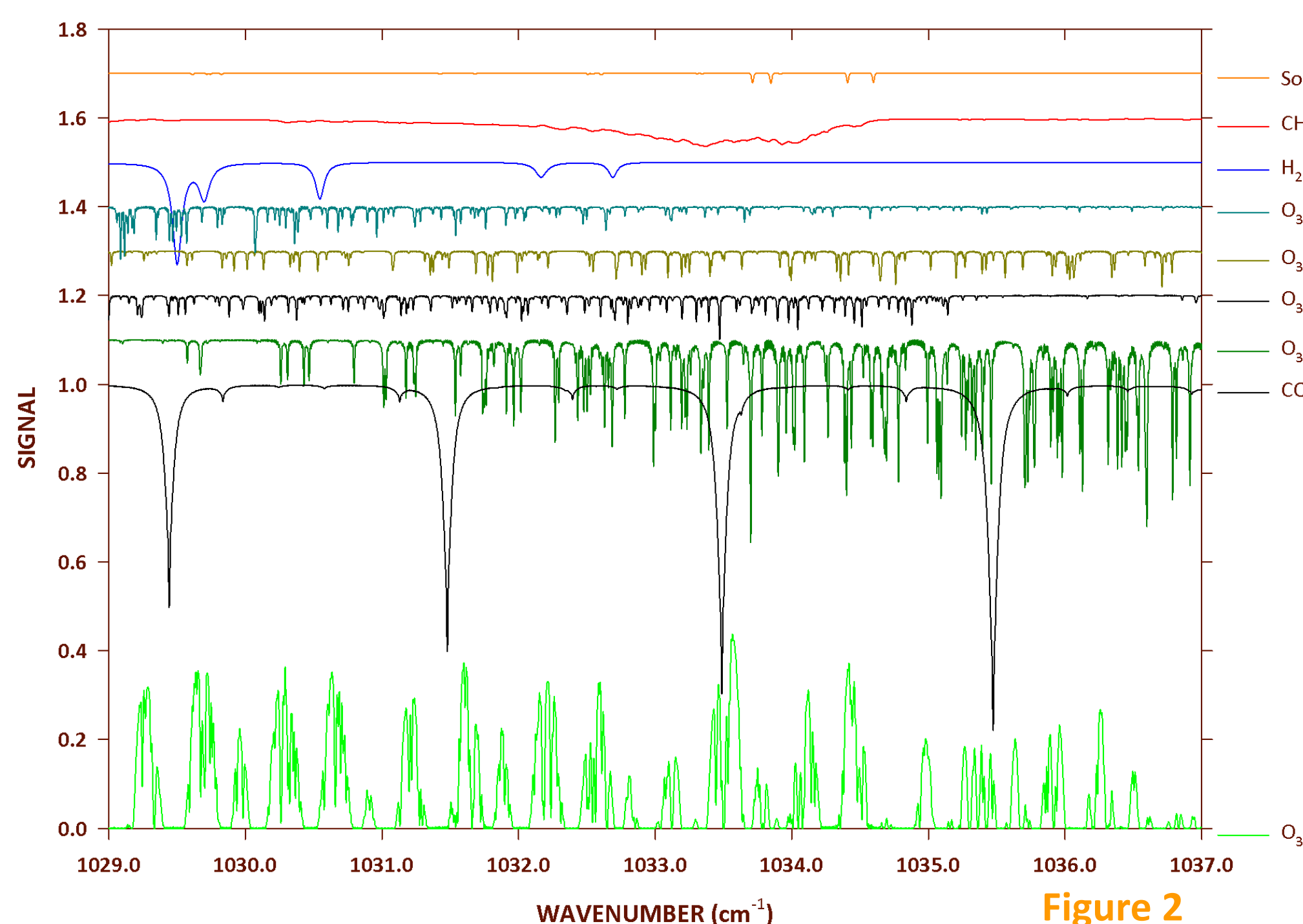
Two synthetic spectra (6.1 mK, zenith angle of 80°) have been computed using HITRAN 2008 and averaged vmr profiles based on the WACCM model climatology. They range from 992 to 1008.3 cm⁻¹ and from 1029 to 1037 cm⁻¹ and both encompass features of the ν₈ band of CH₃OH.

The "1008" window (see Figure 1) limits are issued from the merge of two windows : (i) the one used by Rinsland *et al.* (2009) and the one used by the Atmospheric Chemistry Experiment (ACE) for the retrieval of CH₃OH whose limits are 992-998.7 cm⁻¹ and 995.5-1008.3 cm⁻¹, respectively.

In the "1037" window, on Figure 2, used by Vigouroux *et al.* (2012), absorptions by the main ozone isotopologue (¹⁶O₃, ¹⁶O¹⁶O¹⁶O or O₃) captures nearly 93% of the IR radiation and is close to saturation.

Methanol features are much weaker with respectively an absorption of 0.65 and 1.65% for the "1008" and the "1037" windows.

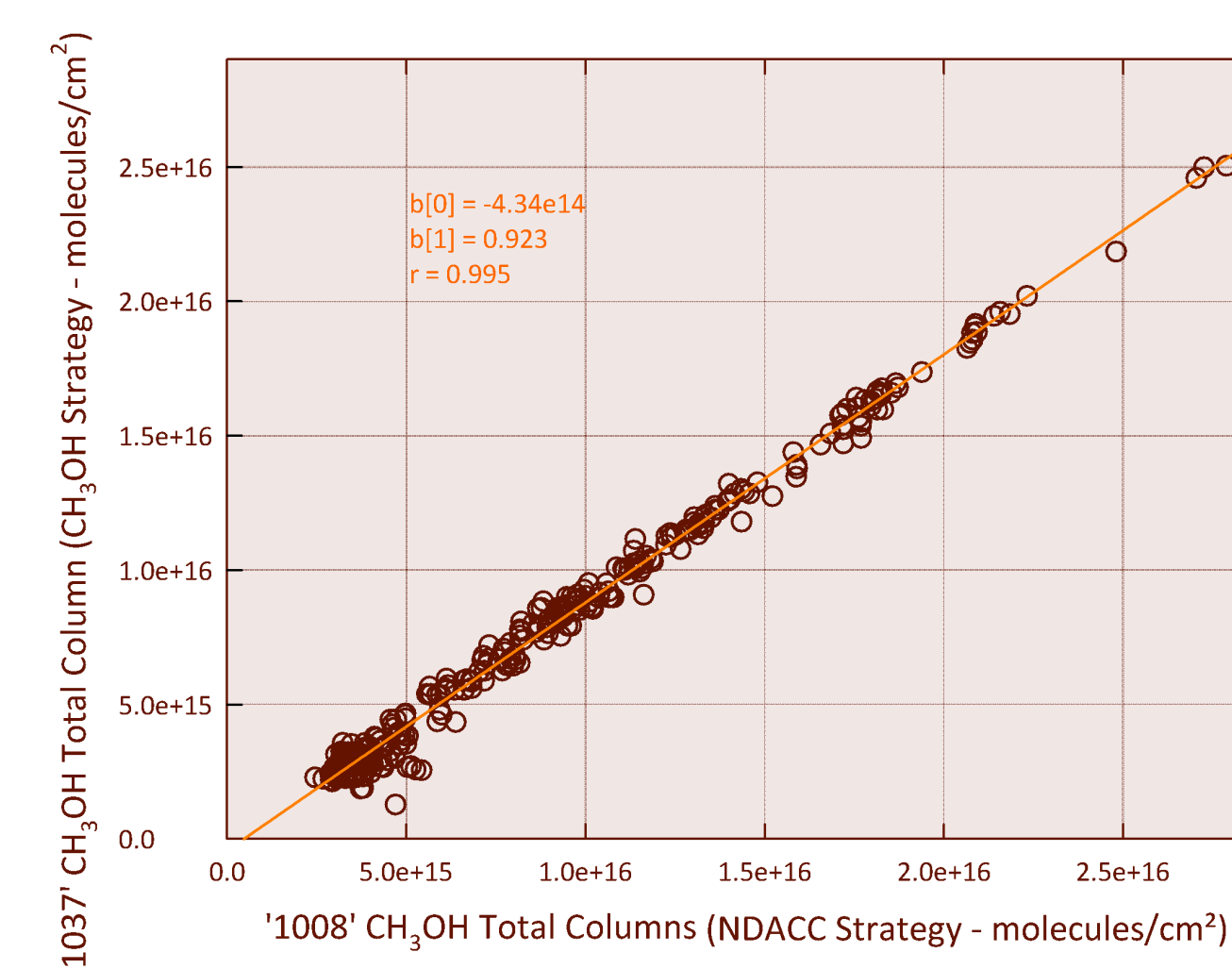
Additional absorptions are associated to O₃ isotopologues, such as O₃(668), O₃(686), O₃(676) and O₃(667) as well as carbon dioxide (CO₂) and water vapour (H₂O).



-B- Optimization - Retrieval strategy and information content

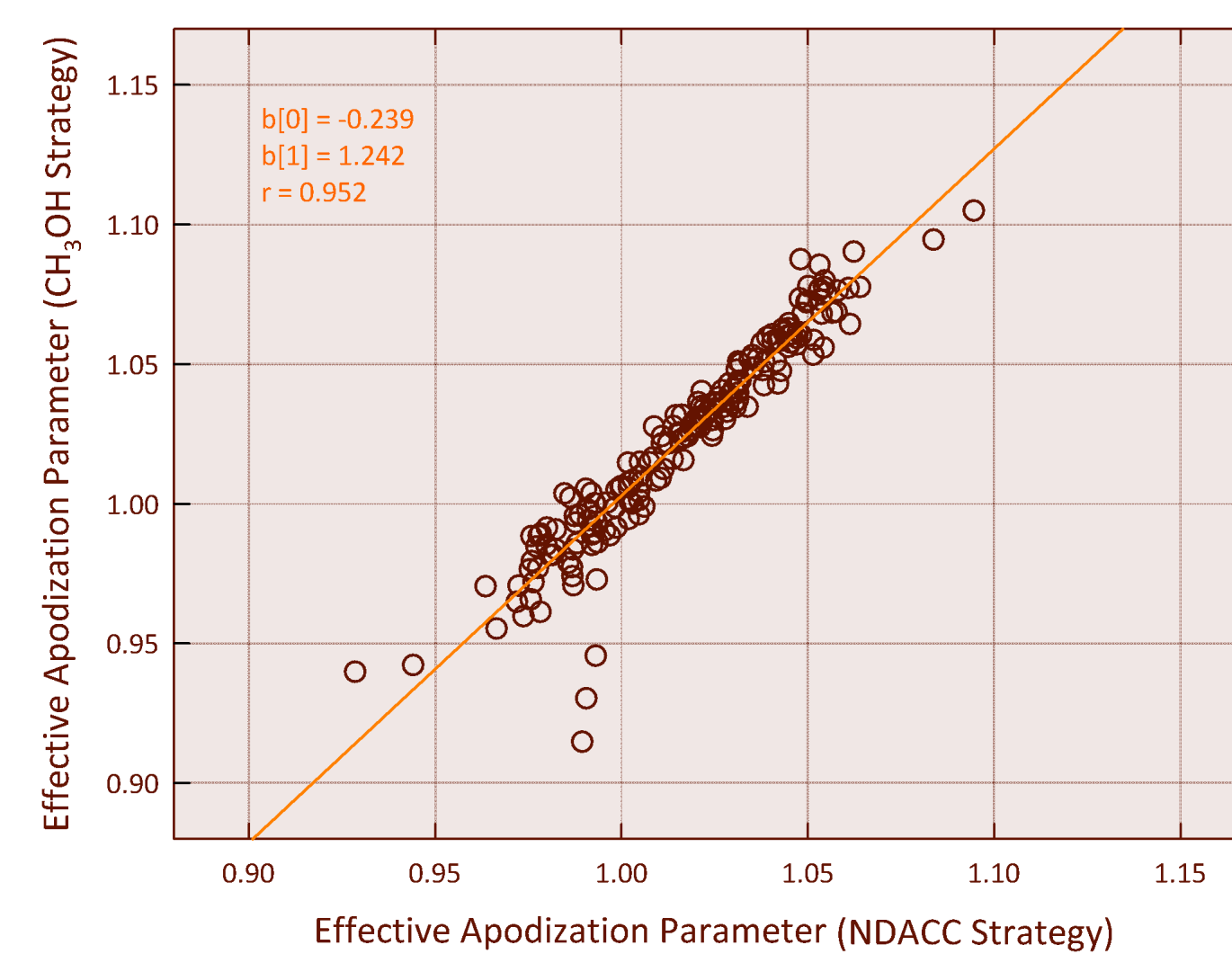
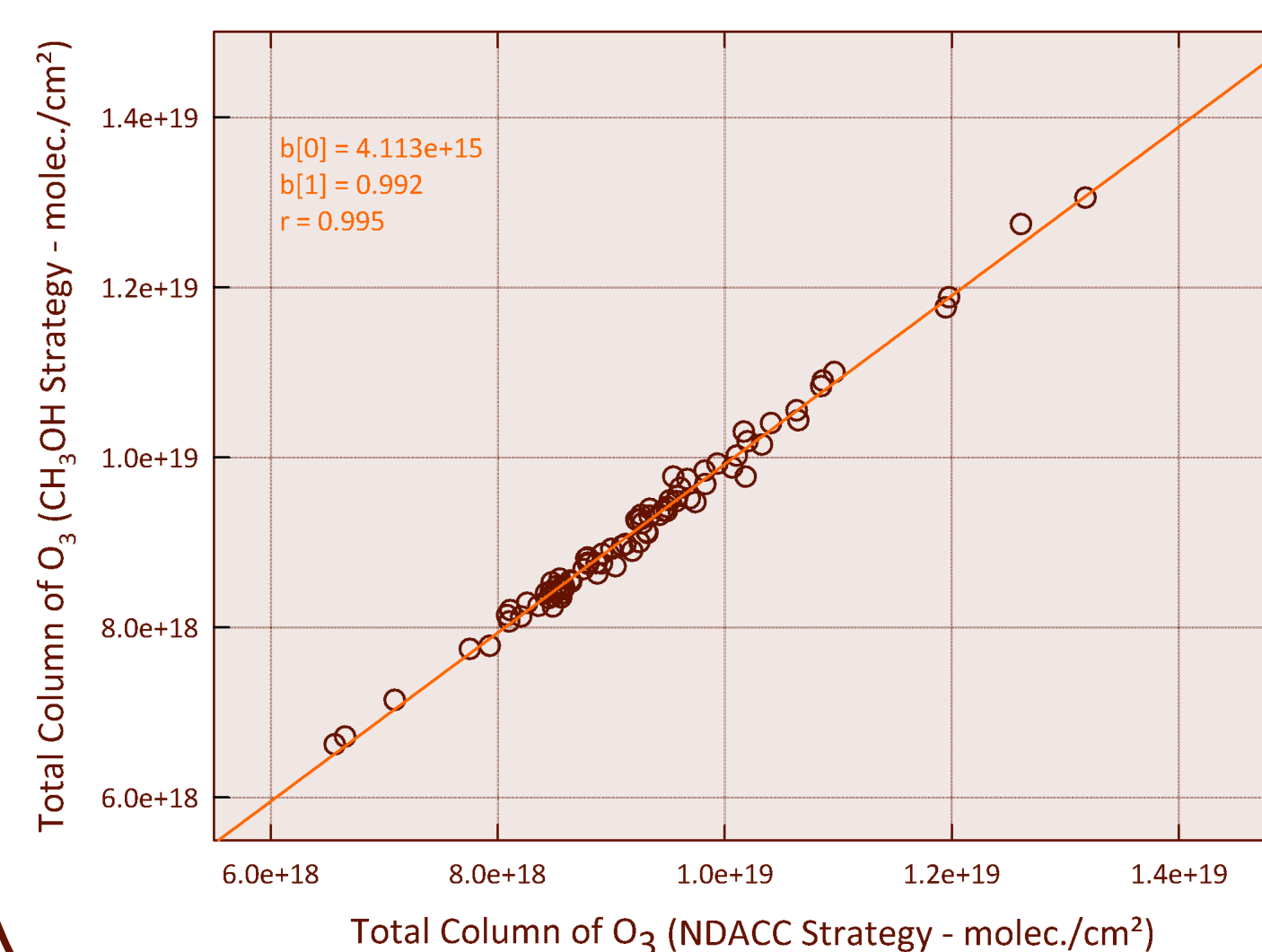
Starting from Mahieu's work (2012), our retrieval strategy has been optimized in order to minimize spectral residuals and maximize degrees of freedom for signal (DOFS), i.e. the number of independent pieces of information that can be retrieved from the observations.

In addition, first results retrieved from our optimized strategy, such as, CH₃OH columns (in both windows), ozone total columns and effective apodization parameter (EAP) as well as comparison with results from the ozone retrieval with the NDACC approach give us good confidence in our results.

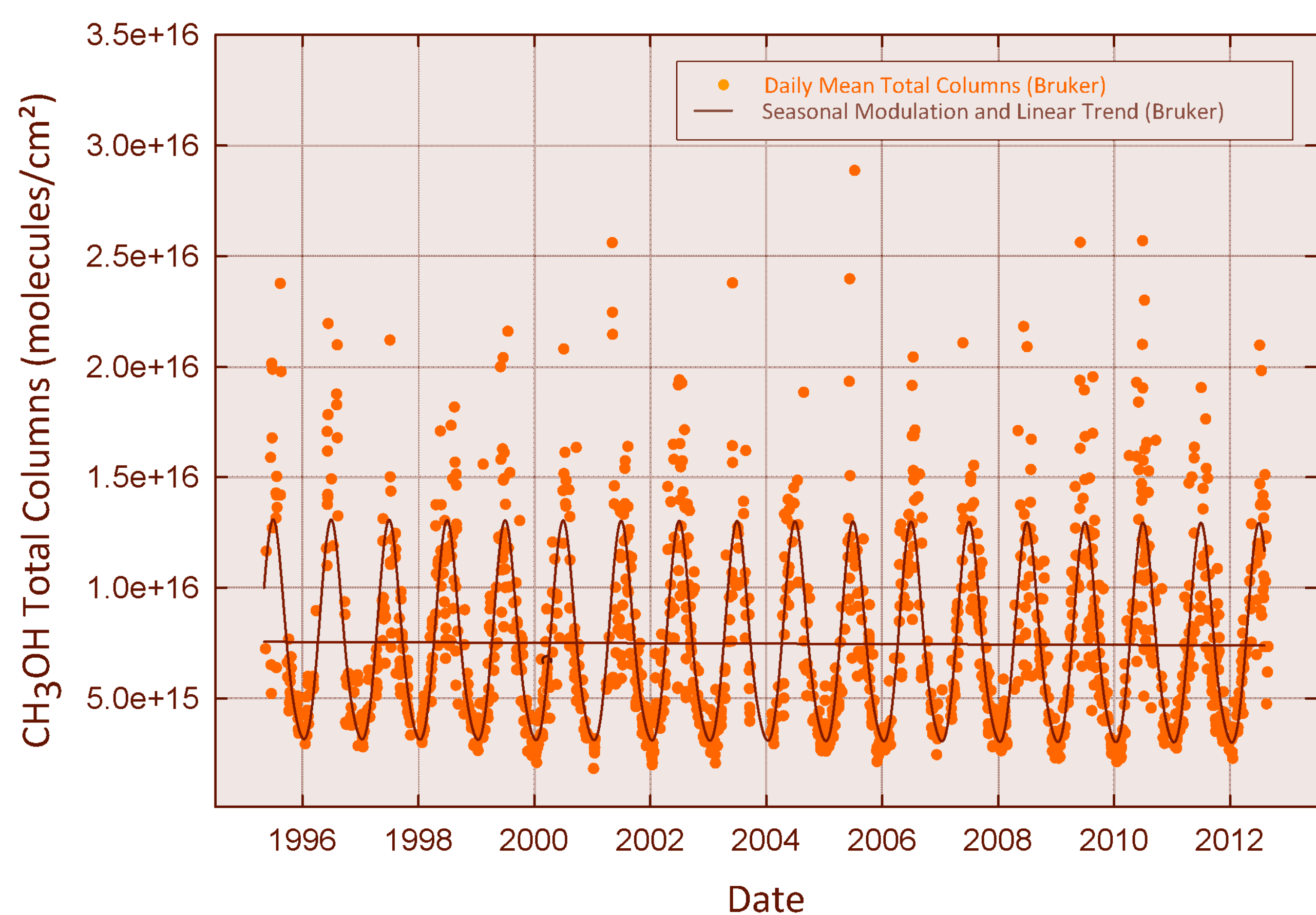


While maintaining an excellent correlation between our two windows, as illustrated on Figure 3, we improved our information content with a mean DOFS of 1.70 (instead of 1.49 in previous work, even 1 in the literature). Since the microwindow used to fit ozone within the NDACC network (namely 1000-1005 cm⁻¹) is included in our "1008" window, we compared our retrieved ozone total columns with the "NDACC" ones on Figure 4. It appears to be no significant bias between the two ozone total columns sets, with a mean relative difference of - (0.008±0.012) % (1-sigma).

The effective apodization parameter provides information on the misalignment of the instrument (EAP = 1.0 = good alignment). Its inversion has been included during both NDACC's ozone retrieval procedures and ours, they are compared on Figure 5 and appear to also show a good correlation.



Methanol Above Jungfrauoch



Retrieval Strategy

All retrievals have been performed with the SFIT2 algorithm (v 3.91) (Rinsland *et al.*, 1998) in order to determine total columns of methanol (see Figure 6 for time series, seasonal modulation and linear trend computed by Gardiner's tool - 2008 -) from a series of about 7 000 spectra recorded between 1995 and 2012 with zenith angles between 60 and 85°. (i) We opted for two spectral intervals ranging from 992 to 1008.3 cm⁻¹ and from 1029 to 1037 cm⁻¹. (ii) The volume mixing ratio (vmr) profiles of CH₃OH, O₃ and O₃(668) are retrieved during the iterative process while the a priori distributions of O₃(686), O₃(676), O₃(667), H₂O and CO₂ are scaled. (iii) As previously determined by Mahieu (*et al.*, 2012), we selected two different values for the signal-to-noise for inversion, i.e. 180 and 40 for the "1008" and "1037" intervals, respectively. (iv) A priori profile for the fitted species are based on the WACCM model climatology (Whole Atmosphere Community Climate Model, see http://www.cesm.ucar.edu/working_groups/WACCM/). (v) We opted for a 50%/km diagonal covariance and a Gaussian half-width for interlayer correlation of 4km for extra diagonal elements. The diagonal covariances adopted for the retrieval of O₃ and O₃(668) profiles are issued from satellite observations and model simulations whose order of magnitude corresponds to that of our observations at the Jungfrauoch. (vi) The HITRAN 2008 compilation was used for the line parameters while (vii) temperature and geopotential height data sets are provided by the National Centers for Environmental Prediction (NCEP, Washington, USA).

Conclusions and Perspectives

Our retrieval strategy has been optimized as the residuals and information content are improved. We delimited our windows and determined their corresponding signal-to-noise ratio. The species whose vmr profiles are retrieved have been settled while the zenith angle range has been enlarged. A first time series has been produced but still requires a thorough error budget characterization and information content analysis. In a close future, we will put more investigations on trends, intra- and inter-annual variations analysis. Results will then be compared to model simulations.

Acknowledgments

The University of Liège involvement has primarily been supported by the PRODEX program funded by the Belgian Federal Science Policy Office, Brussels and by the Swiss GAWCH program. E. Mahieu is Research Associate with the F.R.S. - FNRS. The FRS-FNRS and the Fédération Wallonie Bruxelles are further acknowledged for observational activities support. We thank the International Foundation High Altitude Research Stations Jungfrauoch and Gornergrat (HFSJG, Bern) for supporting the facilities needed to perform the observations. We further acknowledge the vital contribution from all the Belgian colleagues in performing the Jungfrauoch observations used here.

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