Retrievals of ethane from ground-based high-resolution FTIR solar observations with updated line parameters: determination of the optimum strategy for the Jungfraujoch station.

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1. Introduction

- The Ethane (C_2H_6) is the most abundant Non-Methane HydroCarbon (NMHC) in the Earth's atmosphere, with a lifetime of approximately 2 months. C_2H_6 main sources are biomass burning, natural gas loss and biofuel consumption. Oxidation by the hydroxyl radical is by far the major C_2H_6 sink as the seasonally changing OH concentration controls the strong modulation of the ethane abundance throughout the year. Ethane reduces Cl atom concentrations in the lower stratosphere and is a major source of peroxyacetyl nitrate (PAN) and carbon monoxide (by reaction with OH). Involved in the formation of tropospheric ozone and in the destruction of atmospheric methane through changes in OH, C_2H_6 is an indirect greenhouse gas with a net-global warming potential of 5.5 (100-yr horizon).

- All the spectra analyzed here have been recorded at the International Scientific Station of the Jungfraujoch (46.5°N, 8°E, 3580 m asl) with a Bruker IFS-120HR Fourier Transform Infrared (FTIR) spectrometer. It has been put into regular operation since 1984 allowing to record wide-band high-resolution IR solar spectra either with a MCT or InSb detector. 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).

2. Retrieval Strategy

Selected Micro-windows

Parameters have been settled down on the basis of tests on a full year minimizing residuals and maximizing DOFS.

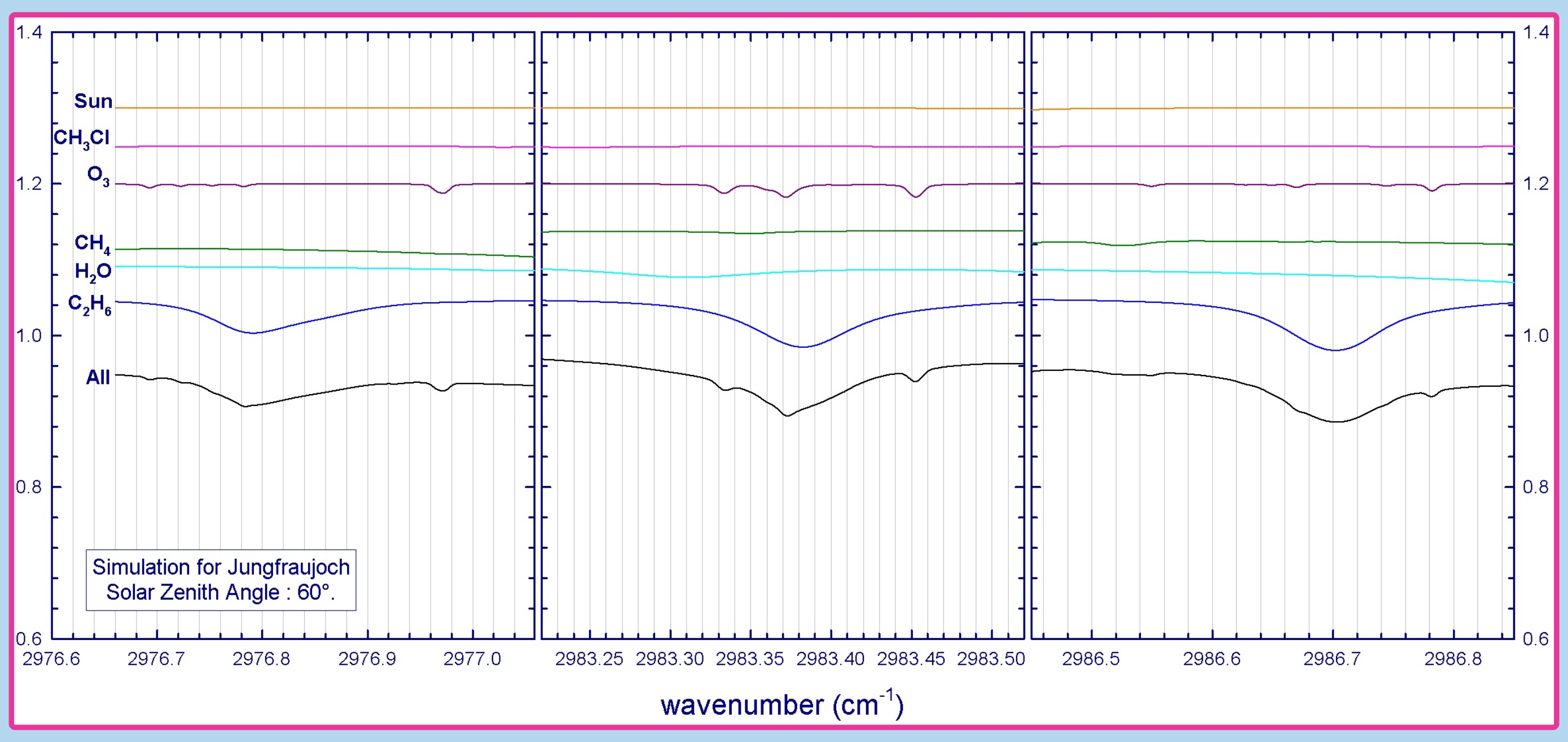
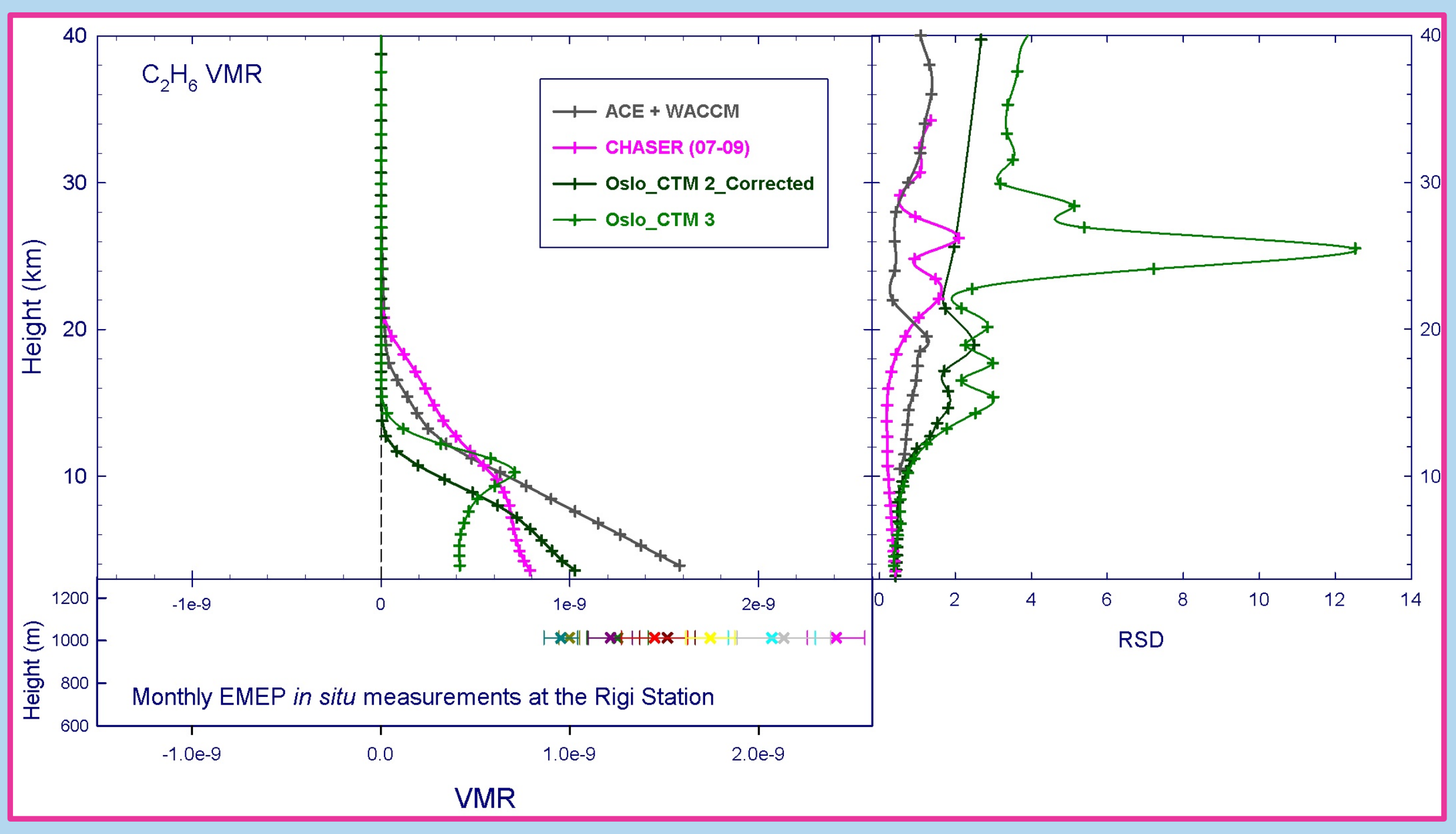


Figure 1 - Synthetic spectra of our three fitted µ-windows (see limits on Table I) for all gases (in black) as well as for the individual contributors (C_2H_6 in blue, H_2O in cyan, CH_4 in green, O_3 in dark pink, CH_3Cl in pink and solar lines in orange) to the absorption in this spectral interval. For clarity, the contributions of each species have been vertically displaced. Simulated solar zenith angle: 60°.

A priori Volume Mixing Ratio (VMR) profiles

We selected the a priori VMR profile among four ethane profiles (see Figure 2) giving retrieved profiles with the least oscillations and least negative VMR values. We also tested those profiles adjusted on EMEP measurements made at the Rigi station (47°N, 8°E, 1031 m a.s.l.).

Figure 2 - The *a priori* profiles tested (left panel) and their associated relative standard deviation (right panel) are illustrated.
The first adopted *a priori* C_2H_6 profile (grey crosses) is a zonal mean (for the 41-51°N latitude band) of 771 occultations recorded by the ACE-FTS instrument between the 2nd of November in 2004 and the 8th of February in 2011 extending from 8.5 to 20 km. The profile extension down to 3.58 km is based on EMEP in situ measurements (bottom panel) while the upper extension to 100 km is based on the WACCM model climatology (Whole Atmosphere Community Climate, http://waccm.acd.ucar.edu). Pink crosses is the *a priori* profile issued from the CHASER 3-D Chemical Transport Model developed at the Center for Climate System Research (CCSR), University of Tokyo/National Institute for Environmental Studies (NIES). Chemical Transport Model v.2 and v.3 from the University of Oslo (Berntsen et al., 1997) are plotted in dark and light green crosses, respectively.



> We selected the a priori VMR profile and their uncertainties issued from the Chemical AGCM for Study of atmospheric Environment and Radiative Forcing (CHASER) Model (Sudo et al., 2002). Residuals were reduced by 7.6 % while DOFS is improved by 17.4 and 11.1 %, in comparison to the Oslo's CTM v2 and v3 a priori profiles, respectively.

Spectroscopic linelist

As the current state of ethane parameters in HITRAN (e.g. : Rothman *et al.*, 2009, http://www.hitran.com) was rather unsatisfactory in the 3 µm region, new ethane absorption cross sections recorded at the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory (Harrison *et al.*, 2010) were combined with HITRAN 2004 line parameters (including all 2006 updates) and therefore used in our retrievals, after conversion into pseudolines by G. C. Toon (personnal communication, 2011). These cross sections were calibrated in intensity by using reference low-resolution spectra from the Pacific Northwest National Laboratory (PNNL, Washington, USA, http://www.pnl.gov/) IR database.

We quantified the impact of two updates of the spectroscopic parameters for both Hitran 2004 and 2008 on spectral residuals (see Table I) :
1. The update of two O_3 lines (encompassed in the 1-$^PQ_3$ µ-window) corrected by P. Chelin (LPMA, Paris, France) in the framework of the UFTIR project.
2. The improvement brought by the update of the line positions and intensities of methyl chloride (CH_3Cl) in the 3.4 µm region (Bray *et al.*, 2011).

Improvements brought by Hitran-08 over the 2004 edition are illustrated on Figure 3.

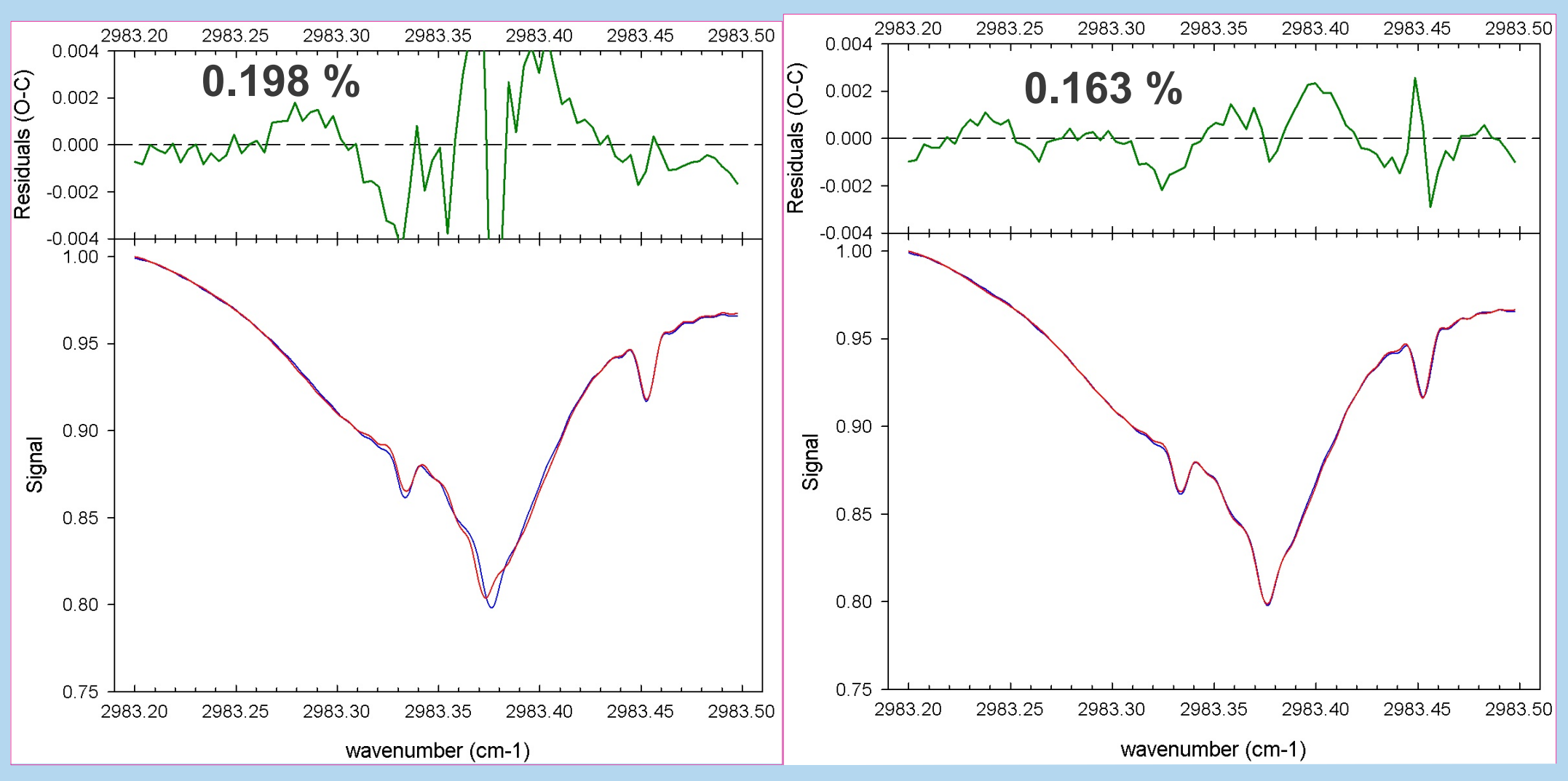


Figure 3 - Mean observed (blue curve)/simulated (red curve) spectra and residuals (green curve) for 187 spectral fits (4.96 mK), using Hitran-04 (left panel) and Hitran-08 (right panel). Harrison's, Chelin's and Bray's updates are used for both.

Table I - RMS Values (in %) for each µ-window (see Table II) according to each linelist tested.

µ-windows	1-$^PQ_3$	u2	u3	Global
1- Hitran-08	0.431	0.206	0.471	0.424
2- Harrison + 1	0.171	0.158	0.173	0.179
3- Chelin + 2	0.169	0.158	0.172	0.179
4- Bray + 3	**0.153**	**0.151**	**0.152**	**0.163**

µ-windows	Limits (cm^{-1})	Interfering species
1 - $^PQ_3$	2976.66 - 2977.059	C_2H_6, H_2O, CH_4, O_3, CH_3Cl
2	2983.2 - 2983.5	C_2H_6, H_2O, CH_4, O_3, CH_3Cl
3	2986.43 - 2986.85	C_2H_6, H_2O, CH_4, O_3, CH_3Cl

Table II - List of microwindows used for our C_2H_6 inversions, for each of them, the third column provides interfering gases adjusted during the retrieval.

Summary

- All retrievals have been performed with the SFIT-2 algorithm (v 3.91) (Rinsland *et al.*, 1998) in order to retrieve three ethane vertical columns (see next frame) on a series of about 13 000 spectra recorded between 1994 and 2011. The adopted settings are : (i) the fitting has been narrowed down to 3 micro-windows described on Table II, (ii) the adopted C_2H_6 a priori VMR profile in all our retrievals, as well as its uncertainties, are based on synthetic profiles produced by the CHASER model for the 2007-2009 time period. A priori profiles for the interfering gases are based on the WACCM model climatology, (iii) HITRAN 2008 line parameters including Harrison's pseudo lines, the two ozone lines update provided by P. Chelin (Personal Communication, 2004) and the updated CH_3Cl lines (Bray *et al.*, 2011) as well as the solar line compilation provided by F. Hase (KIT) have been assumed for target and interfering absorptions, (iv) adopted temperature and geopotential height data sets are provided by the National Centers for Environmental Prediction (NCEP, Washington, USA).

3. Information Content and Error Budget

- Information content and error budget have been carefully evaluated. Figure 4 displays typical results computed for VMR. The first eigen vector and corresponding eigenvalues (see left frame, in red) show that information on both selected C_2H_6 partial columns, namely 3.58-6.79 km (low-tropospheric) and 8.45-14.3 km (Upper Tropospheric-Lower Stratospheric, UTLS), is mainly coming from the retrieval (99 %).

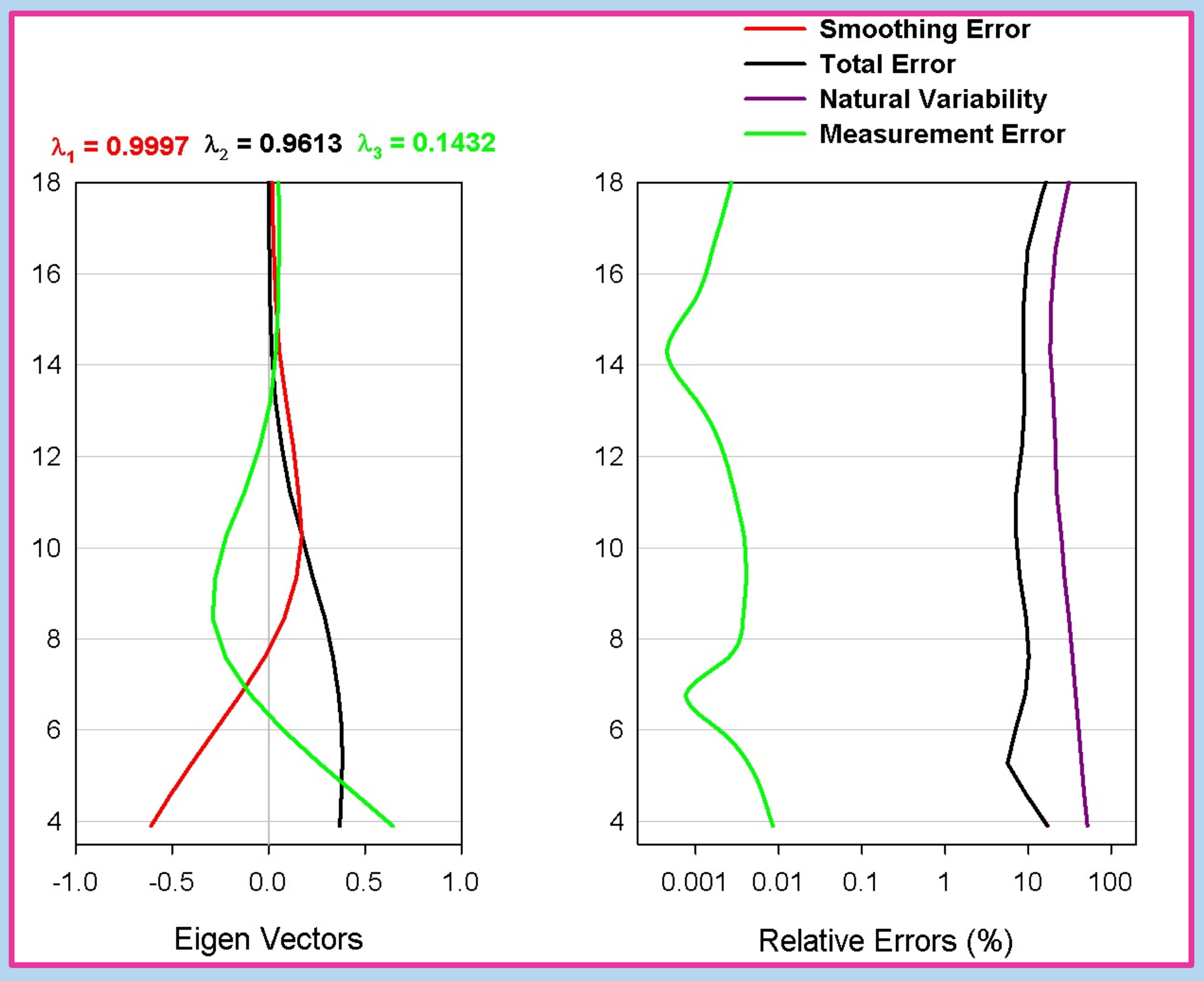


Figure 4 - Information content calculated for typical C_2H_6 retrievals at the Jungfraujoch station. The three first eigenvectors are reproduced in the left frame. Right frame gives the corresponding error budget, with identification of the main error components, together with the assumed variability (see color codes).

- The establishment of a complete error budget is still ongoing. However, preliminary error analysis is displayed on Table III.

Columns		Total	Low-Tropo	UTLS
Solar Zenith Angle		0.04 %	0.16 %	0.14 %
Temperature		0.88 %	3.61 %	3.69 %
Line parameters uncertainties	H_2O	0.10 %	0.29 %	0.18 %
	O_3	0.04 %	0.11 %	0.09 %
	CH_4	0.13 %	0.52 %	0.32 %

Table III - We have already quantified the impact on our retrieved C_2H_6 of the error on the solar zenith angle, on the NCEP temperature profiles and on the line intensities of the interfering species through sensitivity tests. The uncertainties on the solar zenith angle are estimated at 0.2°. Error quantities associated with temperature uncertainties are provided by the NCEP while error on line intensities is provided by uncertainty indices reported on Hitran-04, Rothman *et al.* (2005). Therefore, according to these indices we have included line intensities in our retrievals modified by 2 % for the H_2O lines, by 2 or 5 % for the O_3 line and by 10 % for the CH_4 line. We observe a seasonnal variation of the error as for the error on temperature with a maximum during Spring (10 %) and a minimum (< 0.6 %) during Autumn.

6. Conclusion

- Harrison's new ethane parameters coupled to Hitran 2008 compilation improve the retrieval of ethane in terms of spectral residuals and information content ; as well as Chelin's O_3 and Bray's CH_3Cl updates.
- The selected a priori VMR profiles issued from the CHASER Model gives the least negative profiles with best residuals and DOFS.
- Concerning the long-term trend of C_2H_6, we determined a significant decrease in its concentration over the 1994-2011 time period. We also characterized a seasonnal change in total and tropospheric columns of ethane greater than the previously mentionned decrease. In the UTLS the long-term decrease is as the same order of magnitude than the seasonnal modulation.
- We expect to put more investigations into the study of the interannual variations as well as of the seasonnal change of ethane in the lower-troposphere and in the UTLS region.
- We still have to evaluate the impact of C_2H_6 and CH_3Cl spectroscopy and instrumental line shape in order to refine our error budget.

Acknowledgments

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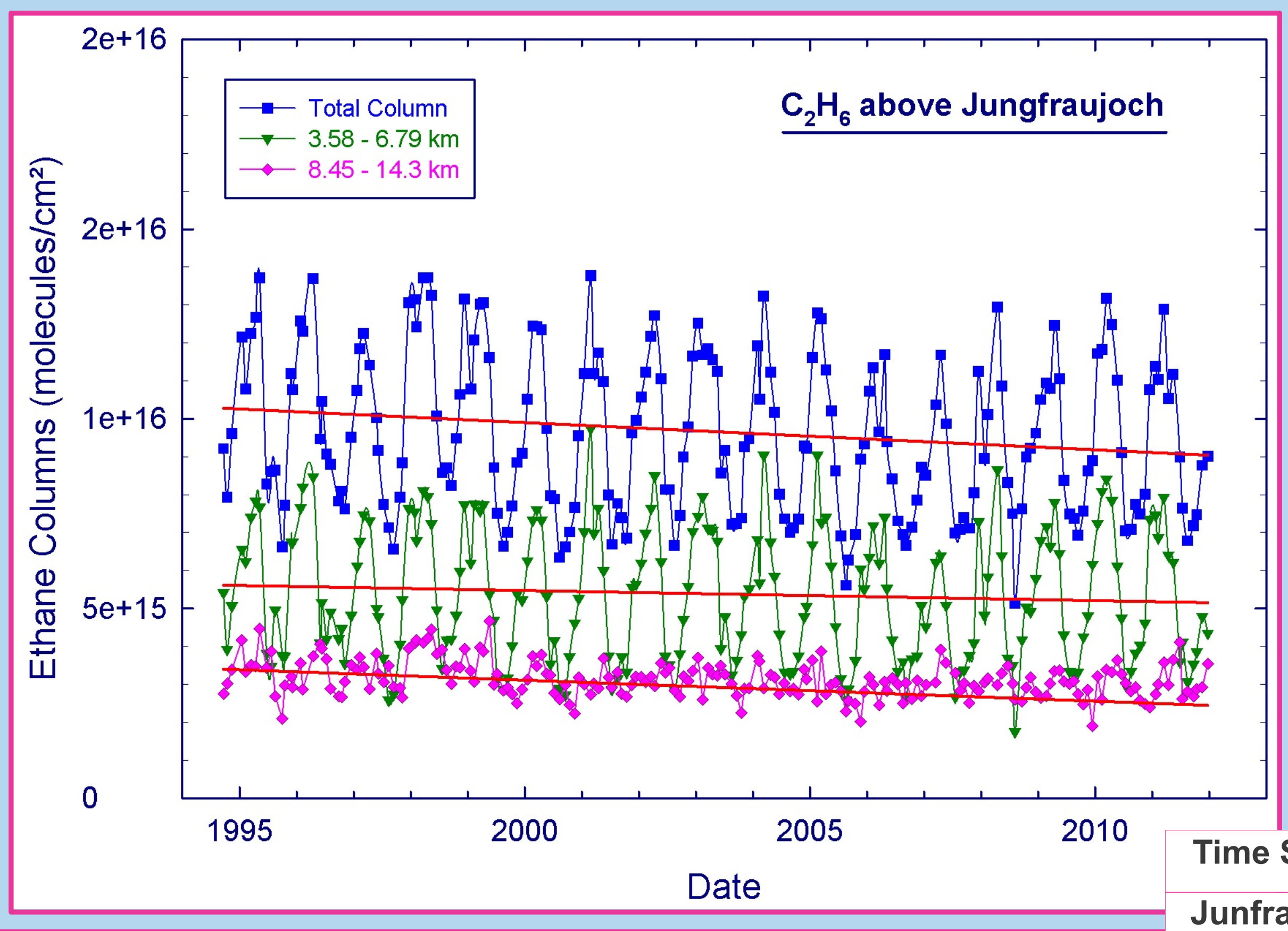
4. Time Series



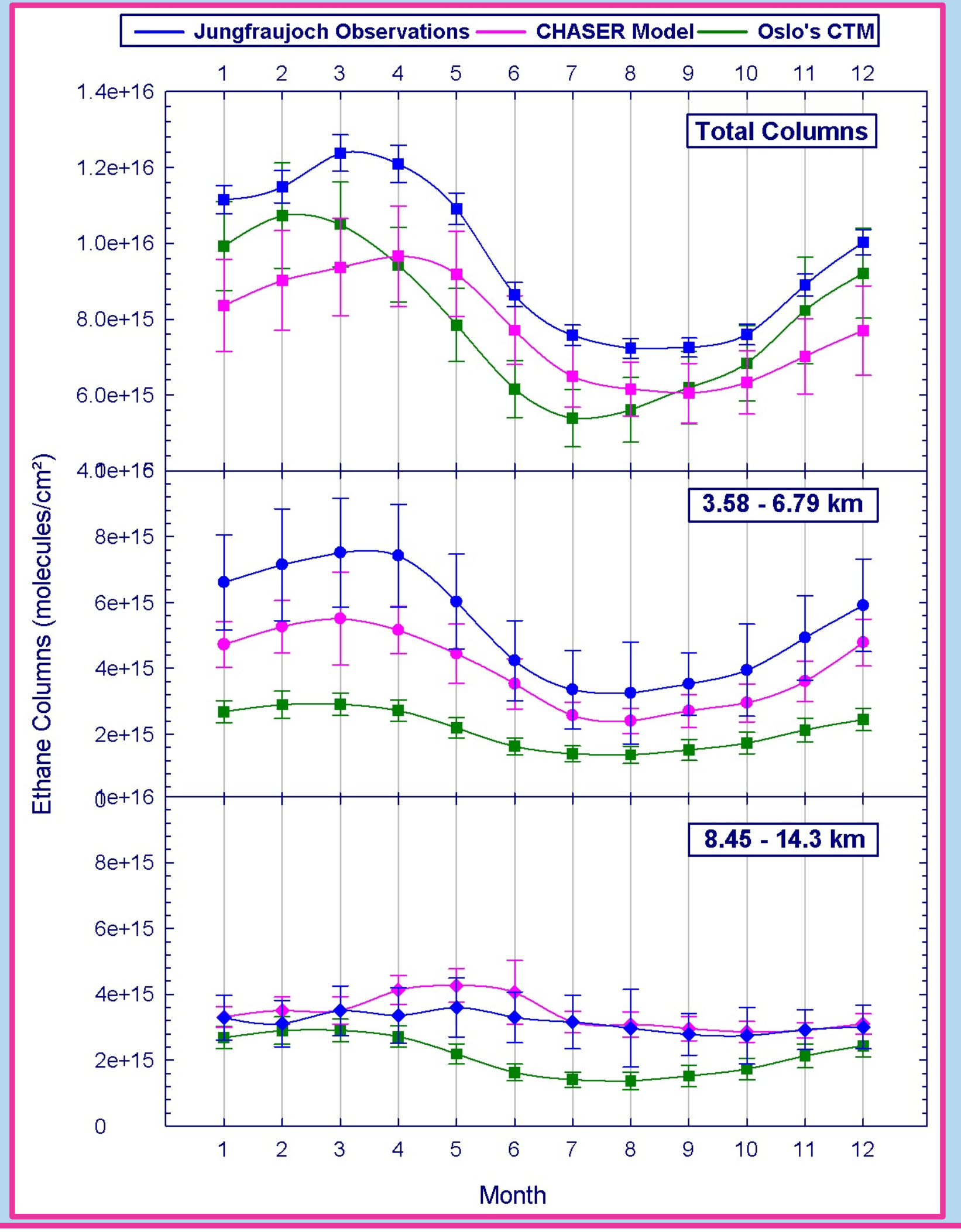
- The Figure 5 displays our retrieved C_2H_6 total column and both partial columns (low-tropospheric and UTLS) above Jungfraujoch. We computed an overall decrease in ethane concentrations since 1994 of -14, -9 and -39 % resp. for our three columns. Trends have been determined using the boostrap resampling tool developed by Gardiner (2008) (see Table IV).
- Our measurements allow to characterize strong seasonal variations of C_2H_6 total and low-tropospheric columns with a maximum generally observed around mid-February. On average, the peak-to-peak amplitudes respectively amount to 50 and 76 % of the 1994 reference column.

Figure 5 - Time series of C_2H_6 total column (in blue), low-tropospheric (3.58-6.79 km, in green) and UTLS (8.45-14.3 km, in pink) partial columns above Jungfraujoch. Red lines are linear trends.

Time Series	Total Column	3.58 - 6.79 km	8.45 - 14.3 km
Junfraujoch (1994-2011)	-0.47 ± 0.35 % (1994)	-0.92 ± 0.30 % (1994)	-0.69 ± 0.24 % (1994)
Jungfraujoch (1994-2008)	-1.06 ± 0.31 % (1994)	-	-
CHASER (1994-2008)	0.55 ± 0.18 % (1994)	-	-
Jungfraujoch (1998-2005)	-1.58 ± 0.68 % (1998)	-0.79 ± 0.98 % (1998)	-2.59 ± 0.89 % (1998)
Oslo's CTM (1998-2005)	-0.89 ± 0.56 % (1998)	-0.72 ± 0.57 % (1998)	-1.26 ± 1.23 % (1998)

Table IV - Annual Change (in %), its 2-σ uncertainties and its reference year for Jungfraujoch, CHASER Model and Oslo's CTM v.3 time series for our three columns.

5. Model Comparison



- On Table IV, we notice a good agreement, significant within 2-σ between Oslo's CTM computed trends and the trends of our retrieved columns.
- On Figure 6, we notice an underestimation of the amount of ethane in the atmosphere by Oslo's model which may be explained by the use of undervalued atmospheric pressures.
- C_2H_6 seasonnal change has been evaluated for both CHASER and Oslo's CTM data with a peak-to-peak amplitude of 35 % (Ref. : 1994) and of 44 % (Ref. : 1998), respectively for ethane total columns. While our low-tropospheric peak-to-peak amplitude amounts to 67 % for the CHASER Model and for 51 % for Oslo's CTM.

Figure 6 - C_2H_6 three columns typical year for Jungfraujoch observations (in blue), results from CHASER Model (in pink) and from Oslo's CTM v.3 (in green). Total columns are respecitvely averaged on the 1994-2011, 1970-2008 and 1998-2005 time periods while CHASER's partial columns are computed over the 2007-2009 time period.

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