

## Impact of different spectroscopic datasets on CH<sub>4</sub> retrievals from Jungfraujoch FTIR spectra

P. Duchatelet (1), E. Mahieu (1), P. Demoulin (1), C. Frankenberg (2), F. Hase (3), J. Notholt (4), K. Petersen (4), P. Spietz (4), M. De Mazière (5) and C. Vigouroux (5)

(1) Institute of Astrophysics and Geophysics of the University of Liège, B-400 Liège, Belgium, (2) Netherlands Institute for Space Research, Utrecht, The Netherlands, (3) Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Germany, (4) Institute of Environmental Physics, University of Bremen, Bremen, Germany, (5) Belgian Institute for Space Aeronomy (BIRA-IASB), Brussels, Belgium.

Due to its high warming potential and its relatively long chemical lifetime (~9 years), atmospheric methane (CH<sub>4</sub>) plays a major role in the radiative forcing responsible of the greenhouse effect. Methane also affects climate by influencing tropospheric ozone and stratospheric water [1]. High quality methane data sets are needed to understand its cycle and evaluate its budget of sources and sinks. Methane vertical distribution as well as total and partial column time series can be retrieved from high-resolution ground-based FTIR spectra, using, e.g., the SFIT-2 algorithm which implements the Optimal Estimation Method of Rodgers [2]. However, although several retrieval approaches characterized by relatively high information content exist, methane retrieved profiles very often present large oscillations in their tropospheric range, which might result partly from inappropriate or inconsistent parameters. Significant improvements on retrieval quality should therefore be reached by using more accurate or compatible CH<sub>4</sub> spectroscopic data. The main purpose of this contribution is to test and compare three different sets of CH<sub>4</sub> spectroscopic parameters and to quantify their impact on CH<sub>4</sub> retrieved products as well as on the fitting quality. Table 1 presents the 5 microwindows simultaneously fitted during the retrieval procedure adopt here. This retrieval approach is also the one selected by the different partners involved in the European HYMN project ([www.knmi.nl/samenw/hymn/](http://www.knmi.nl/samenw/hymn/)).

Limits (cm <sup>-1</sup> )	Fitted species
2613.70 – 2615.40	CH <sub>4</sub> ,CO <sub>2</sub> ,HDO,solar lines
2650.60 – 2651.30	CH <sub>4</sub> ,CO <sub>2</sub> ,HDO,solar lines
2835.50 – 2835.80	CH <sub>4</sub>
2903.60 – 2904.03	CH <sub>4</sub> ,NO <sub>2</sub>
2921.00 – 2921.60	CH <sub>4</sub> ,H <sub>2</sub> O,HDO, NO <sub>2</sub> ,solar lines

Table 1 – List of microwindows used simultaneously for CH<sub>4</sub> inversions. For each of them, the second column provides interfering gases adjusted during the retrieval procedure.

All FTIR spectra inverted in this study, by using the version 3.91 of the SFIT-2 code, are high resolution (0.003 to 0.005 cm<sup>-1</sup>) FTIR solar observations recorded all along the year 2005 at the International Scientific Station of the Jungfraujoch (ISSJ, 46.5°N, 8.0°E, 3580m asl.). Only spectra with solar zenith angle lower than 80° have been analyzed, leading to a subset of about 440 FTIR spectra. *A priori* CH<sub>4</sub> profile and diagonal

covariance matrix used in the retrieval procedure were obtained from zonal means (for the latitudinal band [41-51]°N) of HALOE space-based observations. Below 13 km, the *a priori* CH<sub>4</sub> Volume Mixing Ratio (VMR) profile has however been interpolated downwards to reach CH<sub>4</sub> VMR value close to 1.86 ppm at the altitude site [3].

In the frame of this work, three sets of CH<sub>4</sub> spectroscopic parameters have been tested. The first one is the 2004 version of the HITRAN linelist (reported here after as “HIT-04”) [4]. It’s important to note that the version used here doesn’t include updates available for water vapor lines. However, as water vapor absorptions are quite weak for the microwindow at 2921 cm<sup>-1</sup> at Jungfraujoch, the benefit of using updated H<sub>2</sub>O lines is expected to be marginal in this case. In addition to the original HIT-04 data, recently measured laboratory data have been analyzed in two different ways, leading to two additional linelists for methane. The laboratory work has been performed by Frankenberg *et al.* with a Bruker IFS 120HR Fourier Transform spectrometer (FTS), located at the Institute of Environmental Physics of the University of Bremen [5]. The light of a tungsten lamp, used as the infrared source, passes twice through a 140 cm cell containing the gas mixture and located behind the interferometer, before reaching a liquid nitrogen cooled InSb detector. By dividing sample spectra by spectra obtained without gas cell, transmission spectra were deduced. Furthermore, for the mid infrared range, spectra have been recorded at a temperature of -30°C, in addition to the room temperature. A more complete description of the experimental setup can be found in [5]. Experimental spectra have then been fitted by two different ways: as described in [5], Frankenberg *et al.* have fitted laboratory spectra by applying a multi-spectrum nonlinear constrained least squares approach based on Optimal Estimation: methane spectroscopic parameters so deduced (namely, N<sub>2</sub>-broadened half widths and pressure shifts) were then implemented in the HIT-04 linelist to generate the “CF” dataset. In addition, F. Hase has used the LINEFIT algorithm [6] as forward code to deduce CH<sub>4</sub> line positions and intensities. These parameters were used as updates to the original HIT-04 database, to form the “FH” linelist. These two different fitting procedures have thus led to two additional and original CH<sub>4</sub> spectroscopic datasets, whose impact on CH<sub>4</sub> retrievals are evaluated in this work.

No significant difference on information content (i.e. averaging kernel functions [AvK], their corresponding eigenvectors and eigenvalues, the number of degree of freedom of the signal [DOFS]) has been observed when characterizing our CH<sub>4</sub> retrievals successively performed with the HIT-04, the CF and the FH linelists. VMR averaging kernels (left part of Figure 1) and their corresponding three most significant eigenvectors (middle part of Figure 1) are typical examples of information content results obtained for a solar spectra recorded at mean zenithal angle (65°) and high resolution (0.003 cm<sup>-1</sup>). They show a good sensitivity to methane inversions between the altitude site (3.58 km) and almost 30km. Eigenvalues also indicate that, in that altitude range, the major contribution to the CH<sub>4</sub> retrievals is always coming from the measurement, rather than from the *a priori* state. In addition, when considering the whole timeseries analyzed here, the mean DOFS value is close to  $3.05 \pm 0.27$ , whatever the spectroscopy used. The same conclusion can be drawn when comparing, for each atmospheric layer defined by the AvK functions of Figure 1, individual contributions to the total error of the three most common random error sources (smoothing error, measurement error and model

parameters error): indeed, no significant difference has been observed and, in all cases, the corresponding error budget affecting the retrieved VMRs below 30 km is very similar to the one plotted on the right part of Figure 1. A more deep error analysis of our CH<sub>4</sub> products would include errors associated to methane spectroscopic parameters themselves. However, it was difficult for us to proceed to such analysis, as CF and FH linelists don't provide uncertainties characterizing their methane measurements.

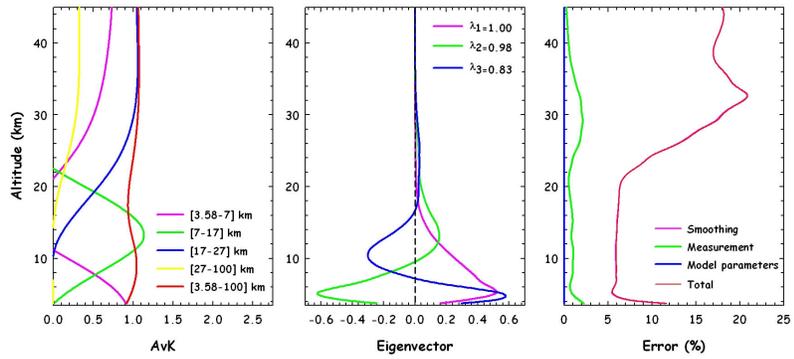


Figure 1 – Typical averaging kernels (AvK, left frame), eigenvectors (middle frame) and error budget (right frame) characterizing our CH<sub>4</sub> retrievals. Calculations have been performed for a spectrum recorded at a solar zenith angle of 65°, with a resolution of 0.003 cm<sup>-1</sup>. The spectroscopy used is the HITRAN 2004 linelist. Very similar curves are obtained while using CF or FH methane spectroscopic parameters.

As can be observed from Table 2 here below, comparisons of retrieved CH<sub>4</sub> total columns using the HITRAN 2004 database with respect to the two other datasets don't show important differences, even if these ones are significant and greater than the total error affecting our retrieved methane total columns. Values reported in Table 2 are mean relative differences over the whole year 2005 computed as [(X-HIT)/HIT]\*100 (%), with X=CF or FH. Corresponding standard deviations on the mean are also indicated. Relative differences for partial columns corresponding to the atmospheric layers defined by AvK of Figure 1 have also been calculated. Once again, bias observed are significant but, this time, are lower than total errors affecting corresponding partial columns. Except for the [3.58-7] km layer, the CF linelist always gives partial columns lower than those obtained with HIT-04. The FH linelist always gives partial columns lower than the HIT-04 ones, except for the [17-27] km altitude range. For both CF and FH linelist, major differences with HIT-04 retrieved columns are observed for the [7-17] km layer.

	<b>X=CF</b>	<b>X=FH</b>
<b>[3.58-100] km</b>	-0.46±0.04	-0.72±0.04
<b>[3.58-7] km</b>	0.85±0.67	-0.63±0.33
<b>[7-17] km</b>	-1.44±0.51	-1.09±0.28
<b>[17-27] km</b>	-0.97±0.61	0.85±0.54

Table 2 – Mean relative differences (computed as [(X-HIT04)/HIT04]\*100) and corresponding standard deviations for CH<sub>4</sub> total and partial columns.

In addition, significant differences and sensitive improvements can be observed when considering CH<sub>4</sub> retrieved VMR profiles. Figure 2 presents retrieval results for a FTIR

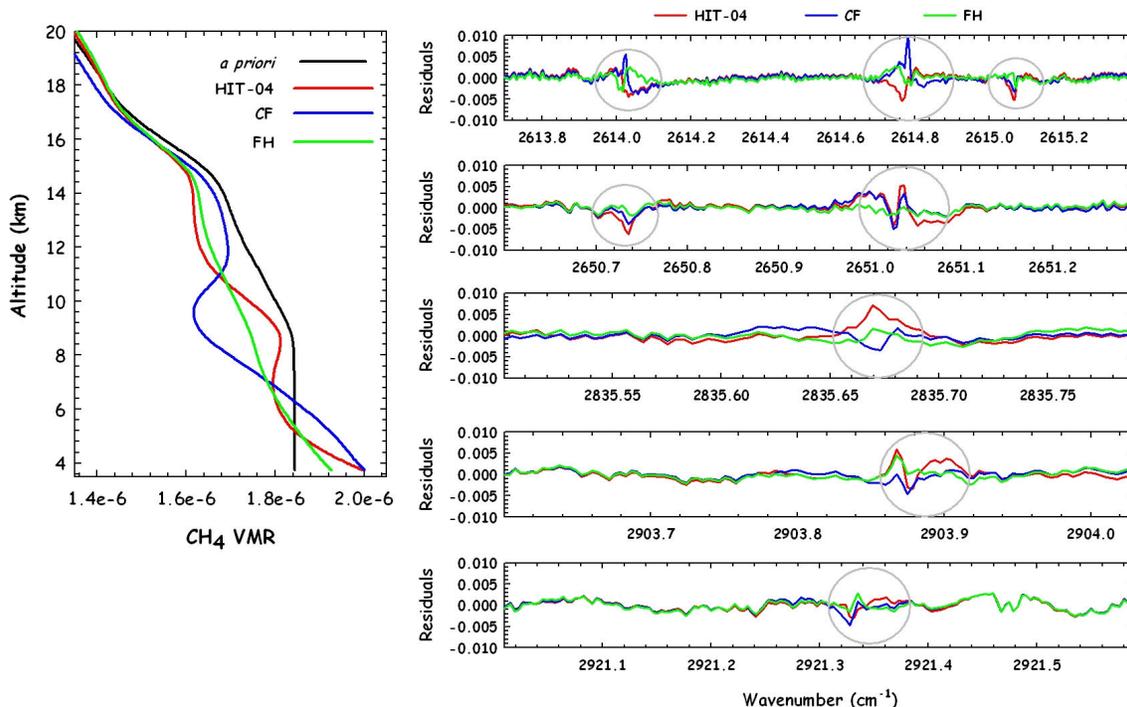


Figure 2 – Example of CH<sub>4</sub> retrieved profiles (left panel) and fitting residuals (right panel) by using the HIT-04, CF and FH spectroscopic linelists. Significant improvements concerning the magnitude of tropospheric oscillations and methane residuals features (grey circles) are reached.

spectrum recorded on March 1<sup>st</sup> 2005, at a solar zenith angle close to 80°. While the CF linelist allows to significantly reduce the magnitude of tropospheric oscillations in the HIT-04 retrieved profile, the FH parameters make them totally disappear (left part of Figure 2). The right part of Figure 2 shows, for each CH<sub>4</sub> microwindow, corresponding residuals (observed minus calculated spectrum). Grey circles indicate residuals structures associated to methane absorption lines. Improvements reached by using CF or FH linelists are clearly visible. To provide a more complete statistics, Table 3 summarizes, for each microwindow, mean residual values averaged over a sample of almost 230 spectra. These values suggest that CF and FH methane parameters significantly improve fitting quality without introducing a large bias on CH<sub>4</sub> retrieved total and partial column (see Table 2).

<b>Microwindow</b>	<b>HIT-04</b>	<b>CF</b>	<b>FH</b>
2613	.0992	.0742	<u>.0661</u>
2650	.1032	.0709	<u>.0620</u>
2835	.1195	<u>.0643</u>	<u>.0705</u>
2903	.1339	<u>.0816</u>	.0901
2921	.1673	.1406	<u>.1377</u>

Table 3 – Mean residuals values (computed over a set of 227 spectra) for each CH<sub>4</sub> microwindow and for the HIT-04, CF and FH spectroscopic linelists. Underlined values give better results for each microwindow.

### References

- [1] World Meteorological Organization, Greenhouse gas bulletin, Bulletin n°2, November 2006.

- [2] Rodgers, C.D., Inverse methods for atmospheric sounding: Theory and Practice, Volume 2 of Series on Atmospheric, Oceanic and Planetary Physics, World Scientific Company Pte. Ltd., 2000.
- [3] GLOBALVIEW-CH4: Cooperative Atmospheric Data Integration Project - Methane. CD-ROM, NOAA ESRL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/ch4/GLOBALVIEW], 2008.
- [4] Rothman, L.S. *et al.*, The HITRAN 2004 molecular spectroscopic database, J. Quant. Spec. and Rad. Transf., 96, 139-204, 2005.
- [5] Frankenberg, C. *et al.*, Methane spectroscopy in the near infrared and its implication on atmospheric retrievals, Atmos. Chem. Phys. Disc., 8, 10021-10055, 2008.
- [6] Hase, F. *et al.*, Analysis of the instrumental line shape of high-resolution FTIR spectrometers with gas cell measurements and new retrieval software, Appl. Opt., 3417-3422, 1999.