Methane spectroscopy in the $2\nu_3$ band

- Implications on atmospheric retrievals from SCIAMACHY onboard ENVISAT -

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Motivation & Introduction

Motivation: SCIAMACHY measurements of CH_4

- The SCanning Imaging Absorption spectro-Meter for Atmospheric CHartographY (SCIAMACHY) on board the ENVISAT satellite was launched on March 1, 2002.

- CH_4 is measured in the short wave infrared (SWIR) between ~1630-1670 nm, covering the Q and R-branch of the $2nu_3$ methane band. Details about the IMAP retrieval algorithm can be found in Frankenberg et al, 2005.

-As the spectral resolution of SCIAMACHY in the methane channel is only 1.3nm FWHM, spectral lines are not resolved and absorptions therefore show a saturation effect which is influenced by pressure broadening of methane transitions.
As these parameters were previously measured only for few transitions in this band, a precise determination for pressure broadening coefficients in the SCIAMACHY retrieval window was the main driver for this study.

-An example of a typical SCIAMACHY NADIR spectra is shown in the lower panel of Figure 1

-Results and data sets shown in this poster are published in
Frankenberg, C., Warneke, T., Butz, A., Aben, I., Hase, F., Spietz, P., and Brown, L. R.: Methane spectroscopy in the near infrared and its implication on atmospheric retrievals, Atmos. Chem. Phys. Discuss., 8, 10021-10055, 2008.

http://www.atmos-chem-phys-discuss.net/8/10021/

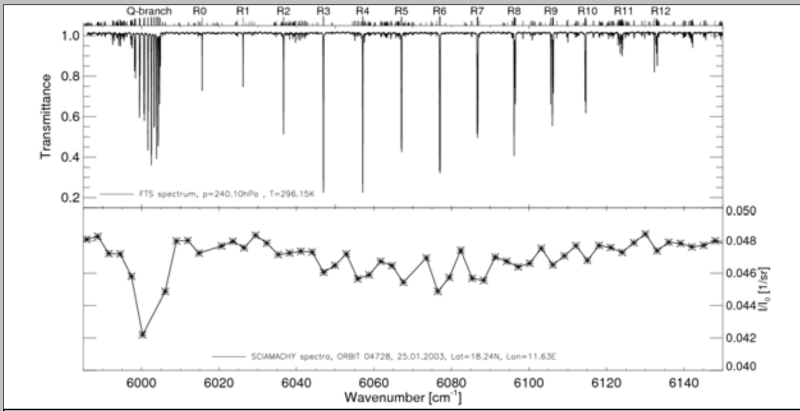

Fig. 1 *Example of a recorded FTS methane transmission spectrum at 240.1 hPa and a SCIAMACHY reflectance spectrum over the Sahara. On top of the plot, a stick spectrum of methane in logarithmic scale is depicted to indicate line positions and strengths. In addition, the attribution to Q and R-branch transitions in the $2nu_3$ band is given. Please note that the SCIAMACHY spectrum is not absolute-radiometric calibrated, so only relative variations should be considered. The major absorber in the SCIAMACHY spectrum is CH_4 but smaller absorptions by CO_2 and H_2O are also present.*

Laboratory measurements and spectral retrievals

Laboratory measurements

Laboratory spectra were recorded over the 5600–6300 cm⁻¹ spectral range with a Bruker IFS 120HR Fourier transform spectrometer (FTS) located at the Institute of Environmental Physics of the University of Bremen. The gas mixtures were introduced in a 140 cm cell. The cell was located behind the interferometer and the light passed twice through the cell before being detected. Transmission spectra were calculated by dividing sample spectra (resolution=0.011 cm⁻¹) by the spectra obtained for the evacuated cell (resolution=0.1 cm⁻¹).Twenty-five interferograms were co-added for the calculation of the spectra. Table 1 (at the right side) gives details about the set of 4 spectra used in this study. N_2 was used as foreign gas.

CH_4 mixing ratio [%]	Temperature [K]	total pressure at start [hPa] at start of scan	increase during scan [%]
≈1.2	295.65	900.0	0.1
≈2	295.65	500.0	0.2
≈2	296.15	239.9	0.2
≈2	297.15	125.7	0.6

Table. 1 Laboratory measurement conditions for the FTS methane spectra. FTS optical path difference was 90cm and gas cell length 140 cm, traversed twice for the measurement.

Multi-spectrum retrievals for the Q and R-branch

We applied a nonlinear fitting approach to derive the spectral line parameters pressure broadening coefficient and pressure-induced shift. Parameters for each individual line were fitted using multiple laboratory spectra simultaneously. Relative line intensities were strictly constrained to the Margolis (1988) values given in HITRAN, permitting only small deviations. Details about the multispectrum fitting technique and its advantages can be found in Benner et al. (1995). Even though the multispectrum approach greatly reduced uncertainty in the retrieval, the inverse problem remained underdetermined as the blended lines cannot be fully separated. For this reason, we added additional constraints using the Optimal Estimation technique (Rodgers, 2000). This approach allowed us to attribute prior uncertainties to the target parameters, thereby minimising oscillations of parameters whose retrieval errors would be strongly correlated in an unconstrained least squares approach.

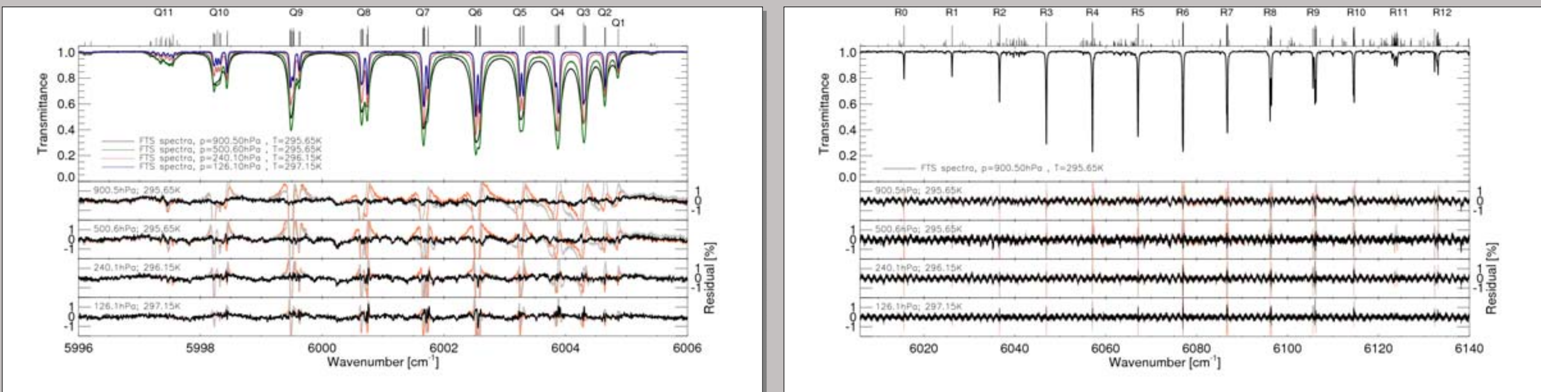

Fig 2. *Fit results of the multi-spectra inversion for the Q (left) and R-branch (right panel). The upper panel depicts the N2 broadened FTS spectra. The lower panels show the fitting residuals for each FTS spectrum separately in black (measured-modeled times 100). The red lines indicate residuals if no changes to the HITRAN database were applied. The gray lines show residuals using the HITRAN database but replacing broadening coefficients with results by Pine (1992, 1997) in the fundamental.*

Results & Discussion

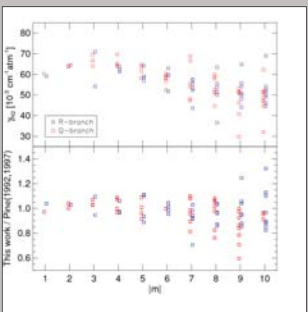

Fig. 3 *Measured N_2-broadening coefficients retrieved in the Q and R branch as a function of |m|. The lower panels depicts the difference of the retrievals as compared to Pine (1992, 1997).*

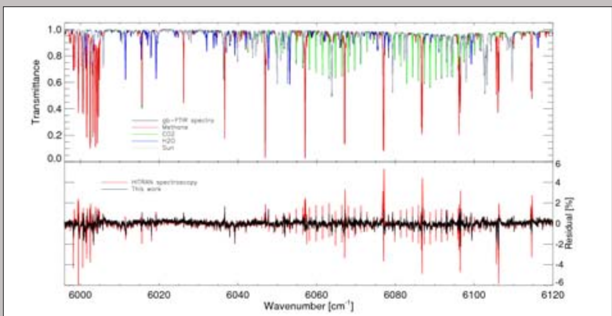

Fig. 4 *Spectral fit of a ground based FTIR measurement in Bremen, Germany, measured with 45 cm optical path difference at 63.51deg SZA on 3 July 2006. The upper panel shows the spectrum and the contributions of the individual gases as well as the sun. The lower panel depicts the fit residuals (Measured-modeled) for the spectroscopic parameters from this study and HITRAN, respectively.*

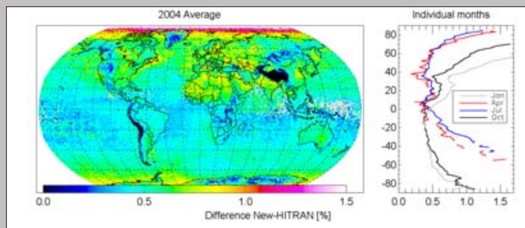

Fig. 5 *Impact of spectroscopy on methane retrievals by SCIAMACHY onboard ENVISAT. The left panel shows the differences averaged over the year 2004 (New spectroscopy – HITRAN spectroscopy) on a 1 by 1 degree grid. The right panel shows the mean latitudinal differences for individual months.*

The retrieved pressure broadening coefficients are, especially at higher J, systematically lower than given in HITRAN and this difference causes systematic effects in both high resolution FTIR retrievals and low-resolution SCIAMACHY retrievals. Examples are shown in Fig 4 and 5 and a more detailed explanation is given in Frankenberg et al, ACPD 2008. Direct sun FTIR retrievals, as in Fig. 4 could also be used as a test-bed for the new spectroscopy in atmospheric conditions. Interestingly, for SCIAMACHY, the change in spectroscopy has almost no effect over highly elevated regions (see Fig. 5) as low maximum pressures and less saturation in general renders erroneous broadening coefficients less crucial. For other regions, a seasonal bias of about 1% can be introduced which is crucial for methane source imversions.

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