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Methods of retrieval of $^{13}CH_4/^{12}CH_4$ and $^{13}CO_2/^{12}CO_2$ ratio in atmosphere using ground-based FTIR spectral measurements

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1. Introduction

High resolution of modern Fourier IR spectrometers (up to 0.001 cm−1) used for remote sensing of the atmosphere makes it possible to distinctly resolve absorption lines of different isotopes of the trace gases.

This paper presents methods and very first results regarding retrieval of $^{13}CH_4/^{12}CH_4$ and $^{13}CO_2/^{12}CO_2$ ratio in atmosphere using ground-based FTIR spectral measurements.

Synthetic atmospheric transmittance spectra in the range of 2200-11000 cm^{-1} were analyzed in order to determine spectral regions with clear features of $^{13}CO_2$ and $^{13}CH_4$ suitable for retrieval of δC_{CO_2} and δC_{CH_4}:

$$\delta C_{CO2} = \left(\frac{(n_{^{13}CO_2}/n_{^{12}CO_2})_{measured}}{R_{standard}} - 1 \right) * 1000‰$$

$$\delta C_{CH4} = \left(\frac{(n_{^{13}CH_4}/n_{^{12}CH_4})_{measured}}{R_{standard}} - 1 \right) * 1000‰$$

where n_{13CO_2}/n_{12CO_2} *and* n_{13CH_4}/n_{12CH_4} are measured ratio of $^{13}CO_2/^{12}CO_2$ and $^{13}CH_4/^{12}CH_4$ concentrations respectively, $R_{standard} = 0.0112372$ is standard $^{13}C/^{12}C$ ratio (PeeDee Belemnite (PDB) standard were used) [1]. List of selected spectral windows is shown in Table 1.

Fig 1. Ural Atmospheric Fourier Station in Kourovka

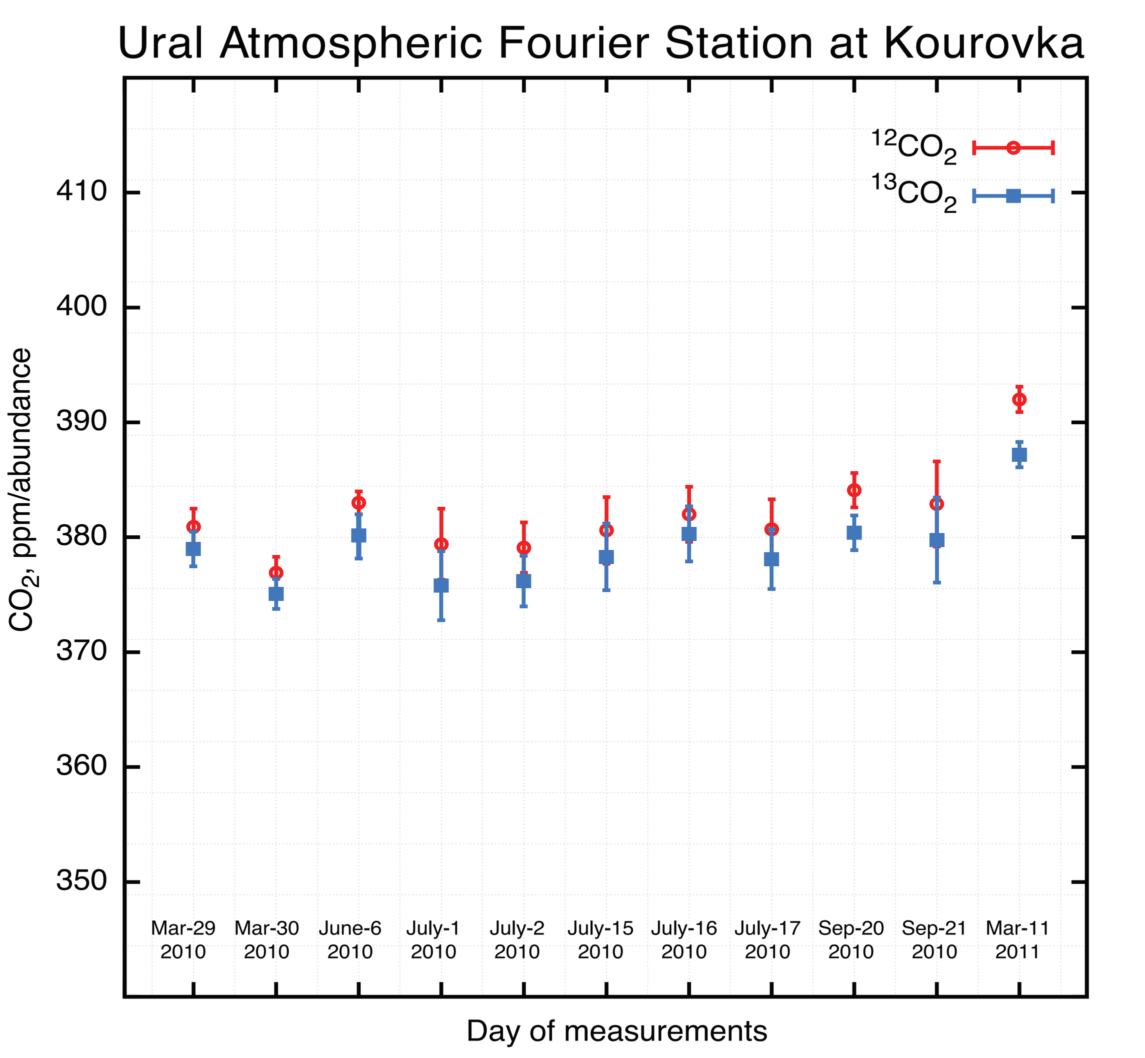

Fig 3. $^{13}CO_2$ and $^{12}CO_2$ constituents measured in UAFS during 2010-2011

2. Experiment

Several atmospheric transmittance spectra measured with ground-based FTIR instruments in Bremen [2] (Germany, 53.104 N, 8.850 E, elevation 27 m)(during March-August 2011) and in the Ural Atmospheric Fourier Station (UAFS) in Kourovka [3] (Russia, 57.038 N, 59.545 E, elevation 270 m, Fig .1) (during March 2010 - March 2011) have been processed in order to retrieve δC_{CO_2} and δC_{CH_4} in the atmosphere.

Spectral fitting was performed using GFIT software provided by TCCON [4]. Standard TCCON windows were used for retrieval of most abundant isotopes of methane and carbon dioxide.

Temperature and H_2O profiles were taken from NCEP/NCAR [5] reanalysis data . For surface pressure and temperature local meteo measurements were used.

Fitting gas	Wave-number cm^{-1}	Window width, cm^{-1}	Other fitting gases *			Line intensity errors from HITRAN2008
$^{13}CO_2$	4898.28	0.70	N_2O	H_2O	$CO^{18}O$	2-5%
$^{13}CO_2$	4899.61	0.60	H_2O	$CO^{18}O$		2-5%
$^{12}CO_2$	6220.00	80.00	H_2O	HDO	CH4	1-2%
$^{12}CO_2$	6339.50	85.00	H_2O	HDO		1-2%
$^{13}CH_4$	2927.60	0.25	$^{12}CH_4$	H_2O		2-5%
$^{13}CH_4$	3000.73	0.30	$^{12}CH_4$	H_2O	O_3	10-20%
$^{13}CH_4$	3001.95	0.30	$^{12}CH_4$	H_2O	O_3	5-10%
$^{13}CH_4$	3006.20	1.40	$^{12}CH_4$	H_2O	O_3	< 1%
$^{13}CH_4$	3007.50	1.00	$^{12}CH_4$	H_2O	O_3	< 1%
$^{13}CH_4$	5921.07	0.15	$^{12}CH_4$	H_2O		2-5%
$^{13}CH_4$	5986.26	0.25	$^{12}CH_4$	H_2O		2-5%
$^{13}CH_4$	6029.20	0.40	$^{12}CH_4$	H_2O	CO_2	2-5%
$^{13}CH_4$	6059.10	0.35	$^{12}CH_4$	H_2O	CO_2	2-5%
$^{13}CH_4$	6068.99	0.25	$^{12}CH_4$	H_2O	CO_2	2-5%
$^{12}CH_4$	5938.00	116.00	CO_2	H_2O	HDO	2-5%
$^{12}CH_4$	6002.00	11.10	CO_2	H_2O	HDO	2-5%
$^{12}CH_4$	6076.00	138.00	CO_2	H_2O	HDO	2-5%

Table 1. List of spectral windows used for retrieval of $^{13}CH_4/^{12}CH_4$ and $^{13}CO_2/^{12}CO_2$

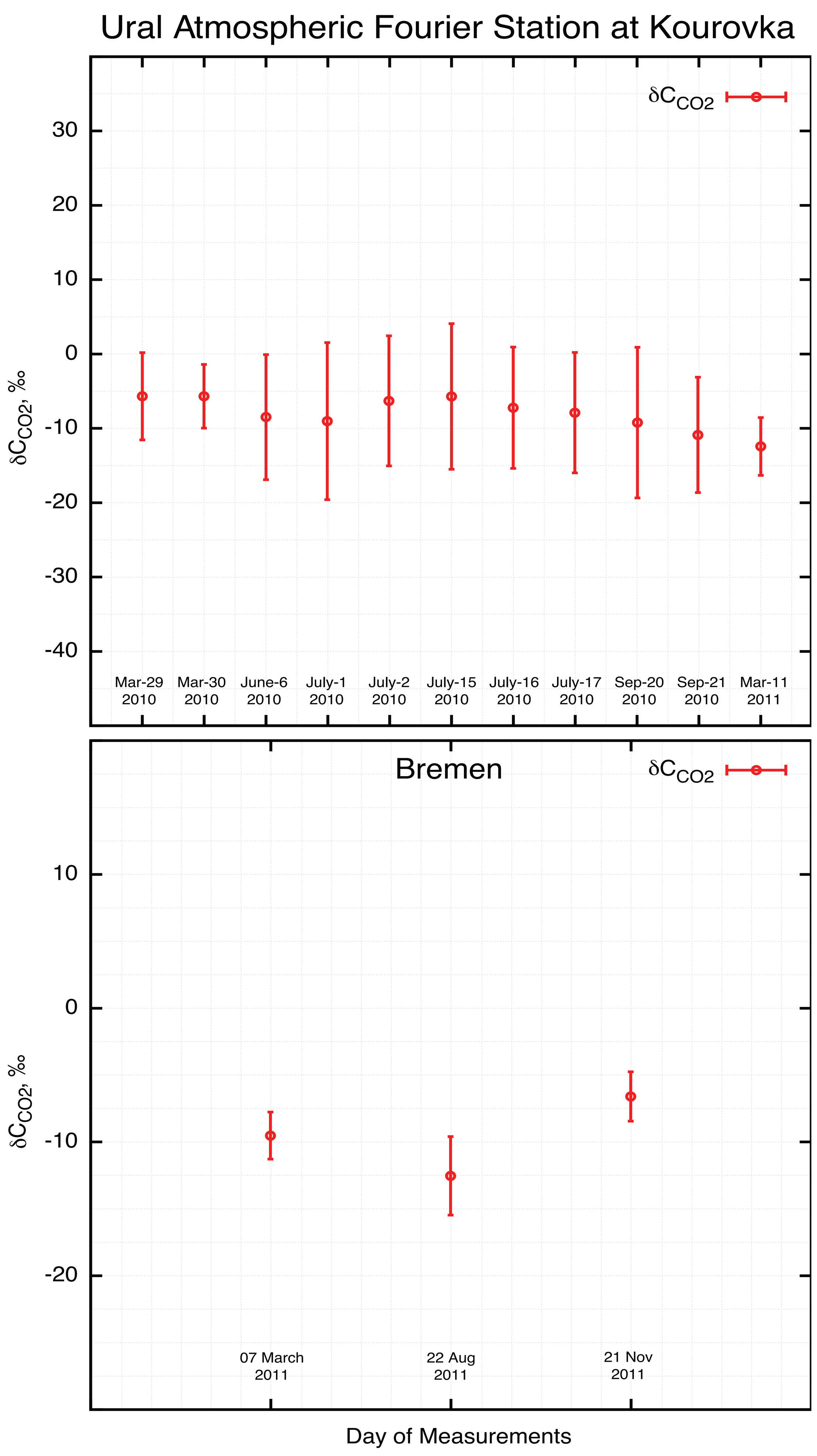

Fig 2. Retrived δC_{CO_2} from UAFS and Bremen measurements

3. Results

As shown in Fig. 2 daily mean values of δC_{CO_2} over Kourovka region varied from (-12.4 ± 3.9) ‰ to (-5.7 ‰ ± 4.3). Mean value of all UAFS measurements is -8.0 ‰. Daily mean values of δC_{CO_2} over Bremen varied from (-12.5 ± 2.9) ‰ to (-6.6 ± 1.8) ‰. Mean value of all Bremen measurements is -9.5 ‰. The obtained results are in agreement with literature data for atmosphere on Northern Eurasia [6]. Fig. 3 shows dry-air mole fractions of $^{13}CO_2$ and $^{12}CO_2$.

Retrieval of δC_{CH_4} was performed only for one-day measurements in Bremen by using spectra from both thermal- and near-infrared regions. Obtained values of δC_{CH_4} varied from (-21.7 ± 15.6) ‰ to (-31.6 ‰ ± 14.7) ‰ with mean value -28.1 ‰ (see Fig. 4). This values look as underestimated in comparison with constituents of $^{13}CH_4$ in natural sources like natural gas and wetlands. Probably the reason of the discrepancy is due to thermal emission effects of the atmosphere and elements of the instrument were not taken into account and because of line intensity errors in spectral line database and the errors in the spectral data. In conclusion it should be noted that in order to obtain statistically representative results much more spectral measurements should be performed.

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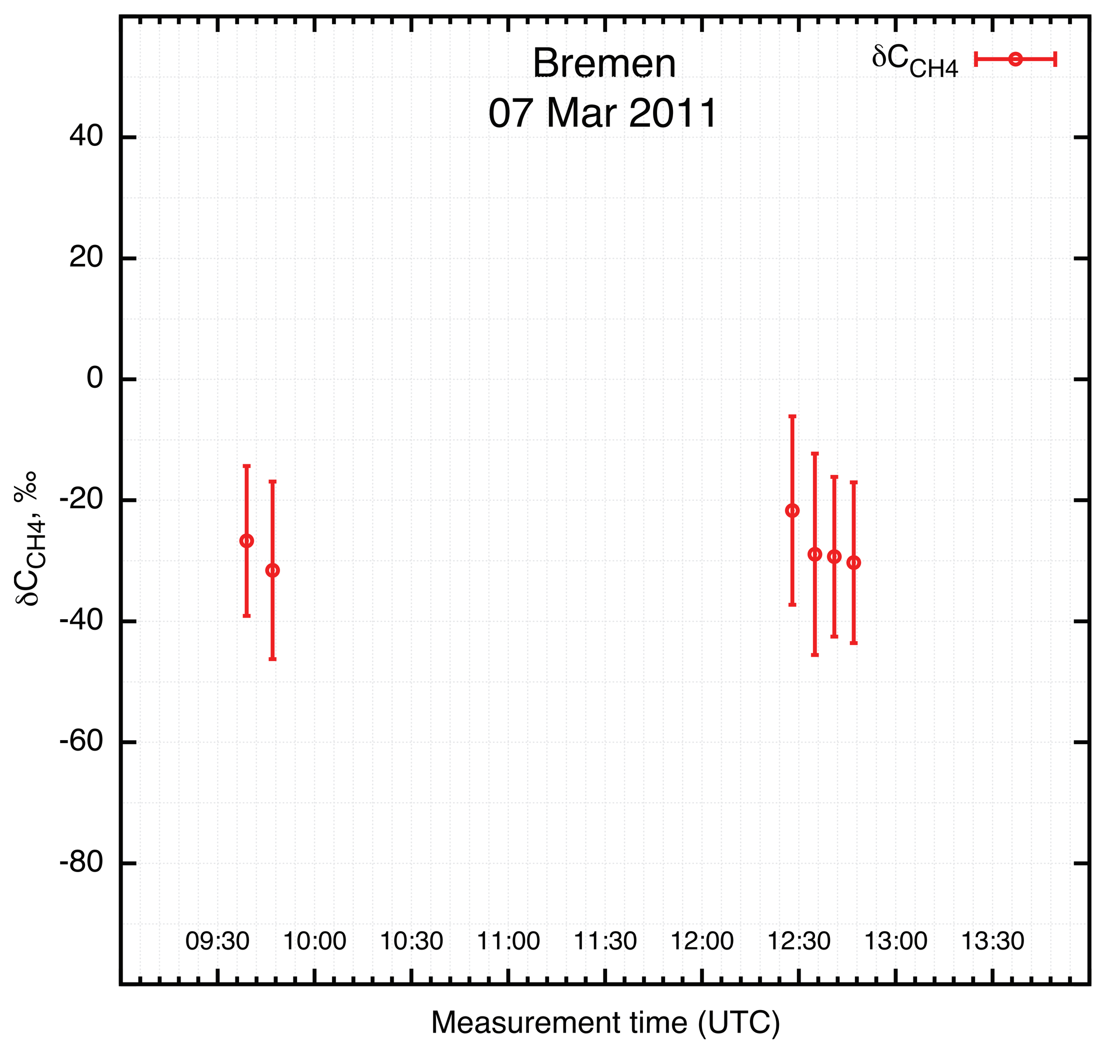

Fig 4. Retrived δC_{CH4} from Bremen measurements 07-Mar-2011