First retrievals of carbon tetrafluoride (CF_4) from ground-based FTIR measurements: production and analysis of the two-decadal time series above the Jungfraujoch

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1. FTIR instrumentation and database

■ Two high resolution FTIR spectrometers operated at the International Scientific Station of the Jungfraujoch (ISSJ; Swiss Alps, 46.5°N, 8.0°E, 3580 m asl) which is part of the Network for the Detection of Atmospheric Composition Change (NDACC; see http://www.ndacc.org).

■ All results presented in this study are derived from the spectrometric analysis of 2027 high-resolution (0.004 cm^{-1} to 0.006 cm^{-1}) FTIR spectra recorded during 686 clear-sky days at ISSJ between January 1990 and December 2010. Signal-to-noise (S/N) ratios vary between 300 up to more than 2500.

2. Retrieval strategy and error budget

■ The analysis of the solar spectra retained here was performed with the SFIT-2 v3.91 algorithm, a code specifically developed to retrieve vertical column abundances and VMR profiles of atmospheric gases from FTIR observations [Rinsland et al., 1998].

■ The investigation is based on three micro-windows and on a two-step retrieval approach. During a first run, a priori VMR profiles of $ClONO_2$ and HNO_3 (two weak interfering gases) are adjusted from two distinct micro-windows extending from 780.00 to 780.355 cm^{-1} and from 868.00 to 868.68 cm^{-1}, respectively. The results from this first run are then used in a second fitting step that encompasses the 1284.73 – 1285.14 cm^{-1} interval, in which the a priori VMR vertical distributions of CF_4, N_2O, $^{13}CO_2$, H_2O (including $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$ and HDO isotopologues), H_2O_2 and HNO_3 are scaled (see Figure 1).

■ The a priori VMR profile adopted for CF_4 is based on nearly 900 solar occultations performed between February 2004 and August 2009 in the 41-51°N latitude belt by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS; Bernath et al., 2005) and is set constant at 72 pptv throughout our model atmosphere.

■ In this study, we have adopted the line parameters of the HITRAN 2004 spectroscopic dataset [Rothman et al., 2005]. However, as this compilation only contains cross-sections for CF_4, we have used the more recent HITRAN 2008 edition for this gas. According to Rothman et al. [2009], this is the first time that a reliable line list is produced and made available for CF_4.

■ Table 1 provides an error budget that characterizes typical individual FTIR CF_4 total column amounts above the Jungfraujoch. These uncertainties were estimated by applying perturbations listed in the last column of Table 1 to a representative subset of spectra. The systematic error contributions result primarily from uncertainties on line intensities which, according to the indices listed in HITRAN files, correspond to 20% and 10 %, respectively for CF_4 and water vapor isotopologues.

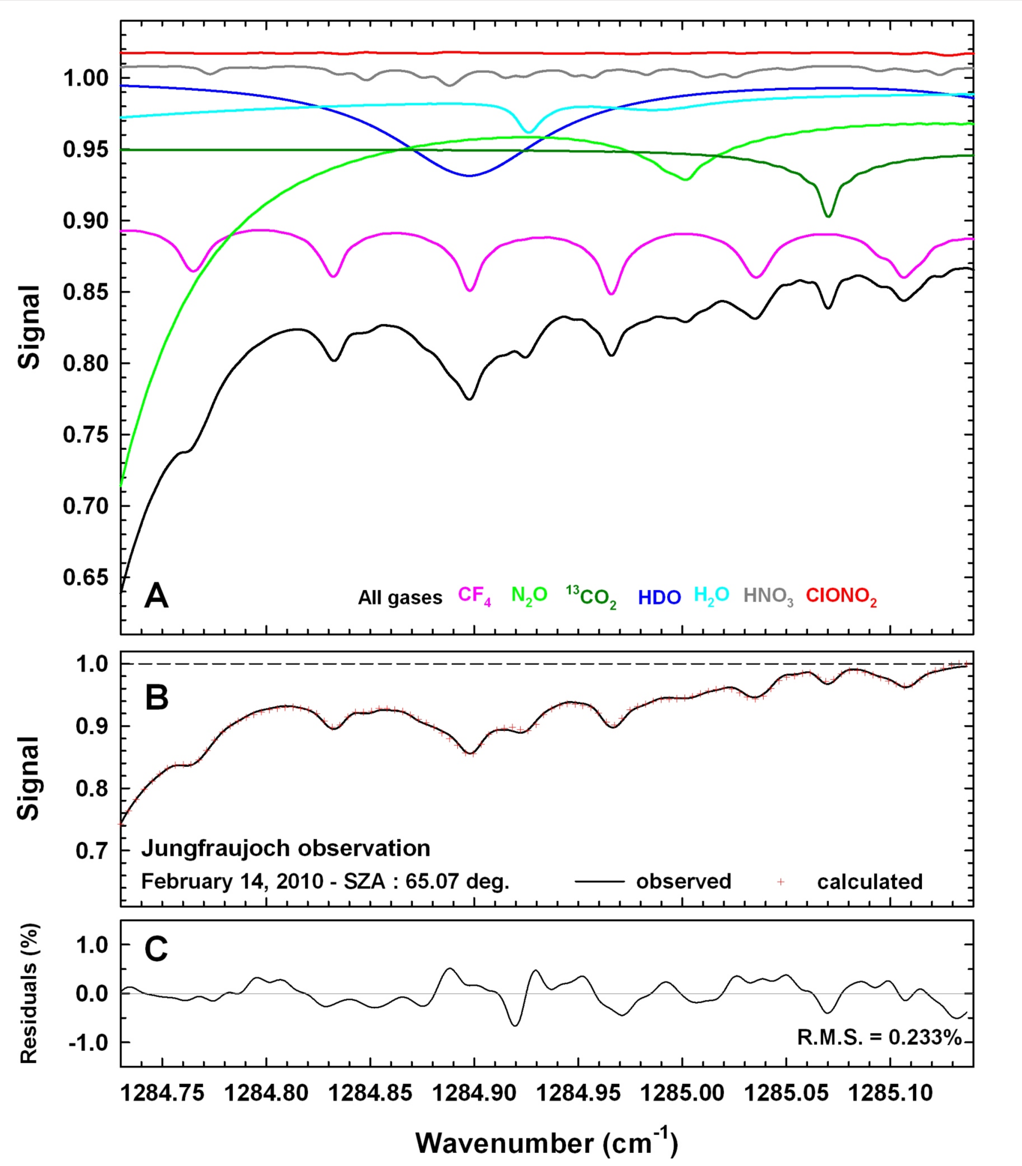

Figure 1 - Frame A: Individual absorptions of CF_4 and of the six more significant interfering gases in the micro-window selected for our CF_4 retrievals (simulated spectrum calculated for a solar zenith angle of 65°). Individual contributions have been shifted vertically for clarity. The H_2O trace combines absorption features of the three isotopologues $H_2^{16}O$ (~1284.93 cm^{-1}), $H_2^{17}O$ (~1284.98 cm^{-1}) and $H_2^{18}O$ (~1284.99 cm^{-1}). Frame B: Typical example of the adjustment with the SFIT-2 code (red crosses) of an FTIR spectrum recorded at the Jungfraujoch on February 2010 (solid black line). Corresponding residuals (observed minus calculated signals) are reproduced in Frame C.

Error source	Max.error value (%)	Comment
Random errors		
Spectra quality	4	Zero offset and S/N
CF_4 a priori profile	<0.5	± 50% variability around a priori
H_2O a priori profile	1	Change by a factor 2 in a priori slope
HDO a priori profile	2	Change by a factor 2 in a priori slope
NCEP T profiles	<1	±4 K around T profiles
TOTAL	**<5**	
Systematic errors		
CF_4 spectroscopy	20	According to HITRAN-08 uncertainties
H_2O spectroscopy	<0.5	Assuming the HITRAN-04 uncertainties (10%)
HDO spectroscopy	<0.5	Assuming to HITRAN-04 uncertainties (10%)
ILS	4	± 10% misalignment assumed
TOTAL	**<25**	

Table 1 - Impact of major sources of random and systematic errors on typical individual CF_4 total column retrievals above the Jungfraujoch.

3. Results and discussion

■ The wettest observations being discarded, the retained individual spectra have led to the CF_4 daily mean pressure-normalized total column time series reproduced in Figure 2, with the error bars representing the 1-σ standard deviations around the means. The long-term trend analysis of this time series was done with a statistical tool developed by Gardiner et al. [2008]. The solid black line of Figure 2 reproduces the linear trend deduced from our complete 1990 – 2010 CF_4 total column time series. All data points (19) outside the 2 black dotted lines of Figure 2, which correspond to the 1-σ standard deviation computed over our dataset, have been considered as outliers.

■ The trend analysis of our CF_4 total column time series reproduced in Figure 2 provides a linear increase above the Jungfraujoch of (1.14±0.04) x 10^{13} molec./cm^2/yr over the 1990-2010 time period. This growth rate is equivalent to a mean global accumulation rate of 13.2±0.4 Gg/yr. Global accumulation rates above Jungfraujoch of 15.4±1.3Gg/yr and of 11.6±0.8 Gg/yr have further been derived for the 1990-2000 and for the 2000-2010 time periods, respectively, and are commensurate with the mean CF_4 emissions rates for the similar time periods deduced from Figure 4 of Mühle et al. [2010]. They additionally confirm the significant slowing in the CF_4 emission rate that took place during the mid-nineties.

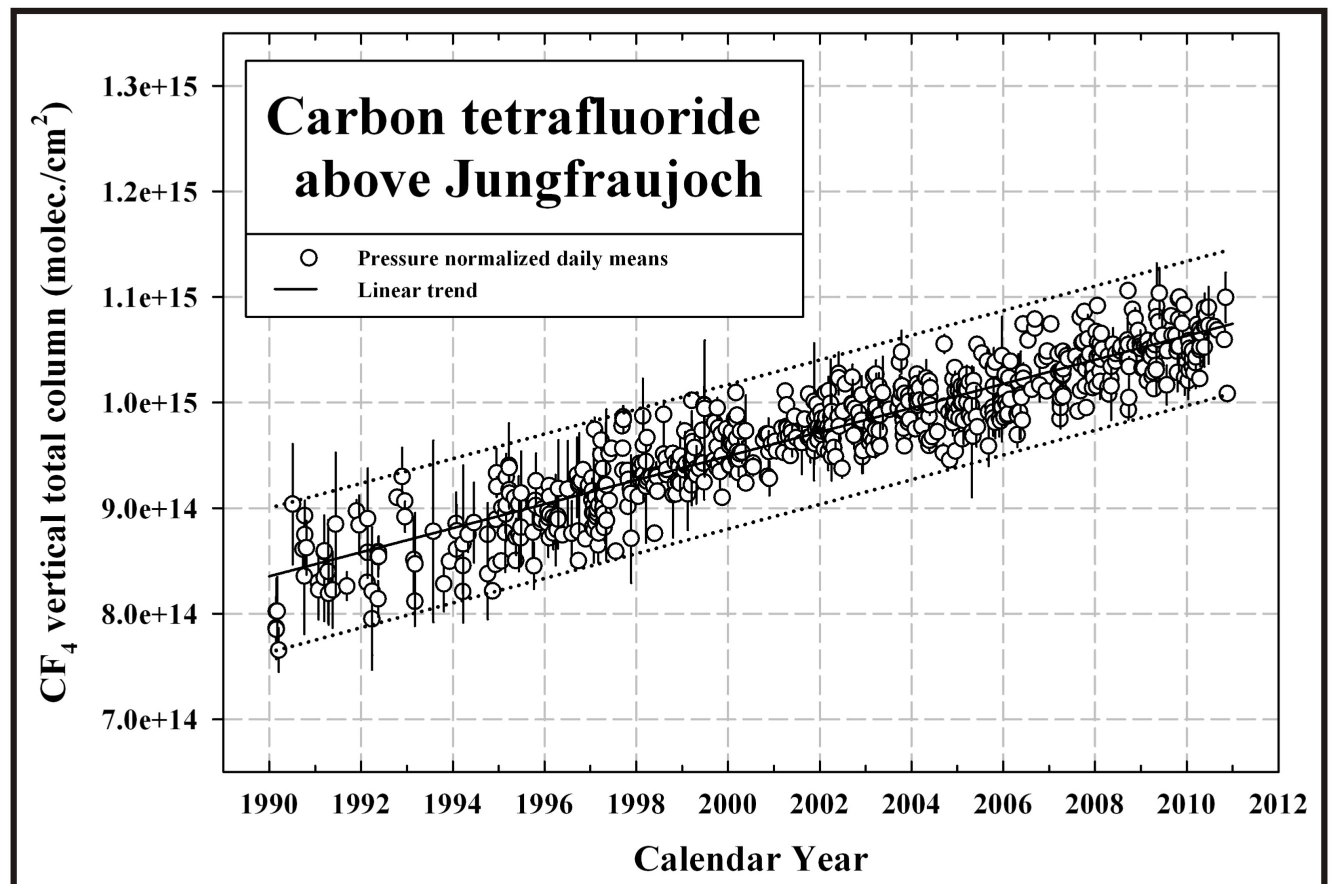

Figure 2 - FTIR time series of CF_4 vertical total abundance above the Jungfraujoch. Data points are daily mean values. Corresponding error bars are 1-σ standard deviations. The solid black line reproduces the linear fit through each data points. The 2 black dotted lines are the limits adopted to filter out our data set (see text for details).

■ In Figure 3, black circles correspond to our FTIR CF_4 monthly mean VMRs above Jungfraujoch. Grey dots are AGAGE simulated monthly CF_4 mixing ratios for the northern extra-tropics (i.e. 30-90°N) by using a lower tropospheric model box [Mühle et al., 2010]. The red up triangles correspond to the CF_4 monthly mean stratospheric concentrations derived from ATMOS v3 measurements [Rinsland et al., 2006] completed with similar CF_4 amounts derived from the ACE-FTS v3 products (red down triangles). Table 2 provides linear growth rates for the 1990-2010 time period corresponding to the trend fits plotted in Figure 3. Based on Figure 3, the mean time delays for concentrations measured by AGAGE (yellow line) to be observed by FTIR (black line) and by ATMOS/ACE-FTS (red line) are close to 5 and 7 years, respectively.

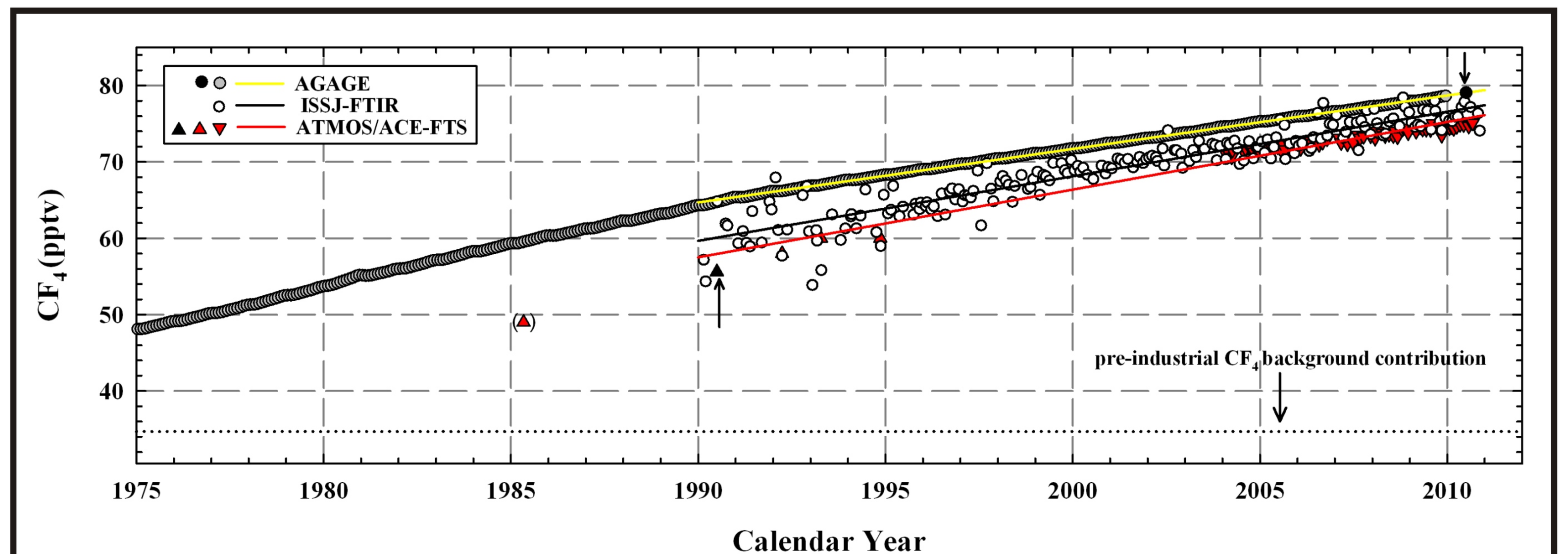

Figure 3 - FTIR (black circles), AGAGE (grey dots) and satellite (red triangles) CF_4 monthly time series. For each data set, solid lines reproduce the 1990-2010 linear trend fit. The black symbols identified with the black arrows are extrapolated values for mid-1990 and mid-2010, respectively, derived from the satellite and the AGAGE time series for the 1990-2010 trend calculation. The 1985 ATMOS data between parentheses has not been included in such trend computation. The horizontal black dotted line indicates the natural contribution to atmospheric CF_4, estimated from AGAGE measurements [Mühle et al., 2010].

Time series	Mean 1990-2010 growth rate (pptv/yr)	Mean 1990-2010 growth rate (%/yr)
AGAGE	0.700 ± 0.002	0.971 ± 0.003
ISSJ-FTIR	0.85 ± 0.04 [0.21]	1.23 ± 0.06
ATMOS/ACE-FTS	0.89 ± 0.05 [0.14]	1.33 ± 0.07

Table 2 - CF_4 linear growth rates for the 1990-2010 time period deduced from each time series of Figure 3 at the 95% precision level. Values between brackets specify errors when the uncertainty on the CF_4 spectroscopic parameters is considered.

4. Conclusions and perspectives

■ FTIR measurements appear to be an appropriate technique for long-term monitoring of the CF_4 atmospheric content and its secular evolution.

■ In order to significantly reduce the uncertainty levels of infrared remote sensing investigations, laboratory work dedicated to a more accurate determination of CF_4 spectroscopic line parameters definitely remains mandatory.

■ With the help of AGAGE CF_4 amounts modeled at higher altitudes, we further plan to quantify more precisely the time necessary for CF_4 to reach the middle stratosphere.

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