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Atmospheric Measurement Techniques Discussions

Spectrometric monitoring of atmospheric carbon tetrafluoride (CF_4) above the Jungfraujoch station since 1989: evidence of continued increase but at a slowing rate

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Abstract

The long-term evolution of the vertical column abundance of carbon tetrafluoride (CF_4) above the high altitude Jungfraujoch station (Swiss Alps, 46.5°N, 8.0°E, 3580 m a.s.l.) has been derived from the spectrometric analysis of Fourier transform infrared solar spectra recorded at that site between 1989 and 2012. The investigation is based on a multi-microwindow approach, two encompassing pairs of absorption lines belonging to the strong ν_3 band of CF_4 centered at 1283 cm^{-1}, and two additional ones to optimally account for weak but overlapping HNO_3 interferences. The analysis reveals a steady accumulation of the very long-lived CF_4 above the Jungfraujoch at mean rates of $(1.38 \pm 0.11) \times 10^{13}$ molec cm^{-2} yr^{-1} from 1989 to 1997, and $(0.97 \pm 0.02) \times 10^{13}$ molec cm^{-2} yr^{-1} from 1998 to 2012, which correspond to linear growth rates of 1.71 ± 0.14 and 1.04 ± 0.02 % yr^{-1}, respectively referenced to 1989 and 1998. Related global CF_4 emissions required to sustain these mean increases correspond to 15.8 ± 1.3 and 11.1 ± 0.2 Gg yr^{-1} over the above specified time intervals. Findings reported here are compared and discussed with respect to relevant results obtained remotely from space and balloons as well as in situ on the ground, including new gas chromatography mass spectrometry measurements performed at the Jungfraujoch since 2010.

1 Introduction

Carbon tetrafluoride (CF_4) or tetrafluoromethane is a perfluorocarbon (PFC-14) whose unambiguous presence in the Earth's atmosphere, from the boundary layer (Rasmussen et al., 1979) to the stratosphere (Goldman et al., 1979), as well as its "near inertness" in the atmosphere (Cicerone et al., 1979) have raised increasing attention and concern among the scientific community since the 1980s.

Its main anthropogenic source is primary aluminum production, during which CF_4 is released through "anode effect" episodes (e.g. Penkett et al., 1981; Khalil et al., 2003). Since the 1980s, non-negligible CF_4 emissions have also been released increasingly

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by manufacturing of semiconductors and other electronic devices (e.g. "plasma etching"; Tsai et al., 2002). The only known but poorly quantified natural sources of CF_4 are of lithospheric origin (e.g. Gassmann, 1974; Cicerone, 1979; Harnisch et al., 1996a; Harnisch and Eisenhauer, 1998; Harnisch, 2000). Recently, Deeds et al. (2008) presented the first in situ evidence for this lithospheric flux, which leads to a background contribution to atmospheric carbon tetrafluoride that lies between 35 and 45 ppt (parts per trillion dry air mole fraction) with the lower value favored on the basis of reported accuracies and precisions (for an overview, see Table 2 of Mühle et al., 2010).

PFCs are long-lived species with lifetimes of many thousand years (e.g. Ravishankara et al., 1993). With an atmospheric lifetime estimated to exceed 50 000 yr, CF_4 is by far the longest-lived PFC (WMO-2010, 2011). Combined with a high global warming potential of at least 7390 on a 100 yr time horizon (WMO-2010, 2011), this compound is a strong greenhouse gas whose anthropogenic emissions are deservedly targeted for regulation under the Kyoto Protocol (IPCC, 2001). In the absence of atmospheric sinks, CF_4 shows a nearly constant mixing ratio profile throughout the atmosphere (e.g. Zander et al., 1992, 1996; Nassar et al., 2006) and its vertical gradient – as quantified e.g. by Fabian et al. (1996), and Harnisch et al. (1996b) using stratospheric balloon-borne cryogenic air sampling between 1987 and 1995 – is only caused by a delayed propagation of the ground-based emissions to higher altitudes. The presence of CF_4 in the stratosphere was first reported by Goldman et al. (1979) who identified the strong ν_3 band of CF_4 at 1283 cm^{-1} in a solar limb spectrum recorded in 1978 at 25 km altitude, from aboard a balloon platform. Its vertical profile between 15 and 50 km was derived by Zander et al. (1987) from ATMOS (Atmospheric Trace MOlecule Spectroscopy; Farmer, 1987) solar limb observations during the Spacelab 3 shuttle mission in 1985, and from subsequent MkIV FTIR balloon flights (Toon, 1991).

Recent ground-level air sampling and in situ measurements of CF_4 in both hemispheres (e.g. Khalil et al., 2003; Mühle et al., 2010) or remotely from space (e.g. Rinsland et al., 2006; Brown et al., 2011) have indicated a significant slowdown in the rate of increase of atmospheric CF_4, attributed to efforts undertaken by the aluminum

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industry to limit its emissions during “anode effect” episodes (International (Primary) Aluminum Institute, 1996, 2009), despite increasing Al production. However, significant uncertainties remain, amongst other due to the increase of Chinese aluminum production and insufficiently defined emissions factors for Chinese smelters. Additionally, the magnitude and temporal evolution of CF_4 emissions from the semi-conductor industry remains very unclear, despite efforts by the World Semiconductor Council to reduce emissions from their industry (WSC, 2013). Based on the inversion with a 2-D box model of a selected subset of AGAGE (Advanced Global Atmospheric Gases Experiment) ground-level measurements in both hemispheres from the early 1970s to 2008, Mühle et al. (2010, Fig. 4) derived global CF_4 emissions which increased during the 1970s to reach their maximum during the early 1980s ($17.5 \pm 1\,Gg\,yr^{-1}$) and subsequently declined progressively to stabilize at about $11\,Gg\,yr^{-1}$ by 2000 until 2008. We refer the reader to Mühle et al. (2010) and references therein, for a detailed and exhaustive discussion regarding the evolution of CF_4 in the global troposphere from 1973 to 2008.

This paper reports on the mean evolution of the vertical carbon tetrafluoride loading integrated over the free troposphere and stratosphere above the high altitude Jungfraujoch station, derived from the spectrometric analysis of Fourier transform infrared (FTIR) solar observations made at that site between 1989 and 2012. Related findings are compared with relevant ones also obtained remotely from space- and balloon-borne solar observations, with new in situ gas chromatography mass spectrometry (GCMS) measurements performed by Empa (Laboratory for Air Pollution/Environmental Technology) at the Jungfraujoch since 2010, as well as with recently reconstructed in situ ground level baseline growth rates of CF_4 in both hemispheres, reported by Mühle et al. (2010). Our concluding remarks include recommendations for improving the relative accuracies of spectroscopic CF_4 line parameters which currently remain estimated at ±6 %, as compared to the achieved 1–2 % for the in situ data.

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Since 1990, the University of Liège research activities at the Jungfraujoch are performed within the frame of the Network for the Detection of Atmospheric Composition Change (NDACC; see http://www.ndacc.org).

2 Instrumentation and original datasets

2.1 FTIR remote-sensing measurements and retrieval strategy

The long-term CF_4 time series presented and analyzed in this study has been derived from the analysis of solar spectra recorded between January 1989 and December 2012 under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (hereafter ISSJ; Swiss Alps, 46.5° N, 8.0° E, 3580 m a.s.l.). The recordings were made with two very high spectral resolution FTIR spectrometers, a "home-made" instrument primarily used until 1995, and progressively replaced by a faster, more sensitive commercial Bruker-120 HR instrument (Zander et al., 2008).

The observational database investigated here consists of over 5500 spectra recorded with an optical filter covering the 750 to 1400 cm^{-1} spectral region, thus encompassing the strongest infrared band of CF_4 – the ν_3 centered at 1283 cm^{-1}. Spectral resolutions (defined as the reciprocal of twice the maximum optical path difference) alternate between 0.004 and 0.006 cm^{-1}, depending on the rate of solar zenith angle variation during the day, and scanning time of successive recordings. Signal-to-noise (S / N) ratios vary between 150 to more than 2500 (average spectra resulting from several successive individual Bruker scans, predominantly around mid-day, when solar zenith angles vary slowly).

The spectral analyses were performed with the SFIT-2 v3.91 fitting algorithm, a code based on the optimal estimation formalism of Rodgers (1976) and specifically developed to retrieve vertical column abundances and mixing ratio profiles of atmospheric gases from FTIR observations (Connor et al., 1995; Rinsland et al., 1998). This code has been successfully intercompared with the PROFFIT retrieval algorithm (e.g. Hase

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et al., 2004; Duchatelet et al., 2010), the other tool in use in the NDACC FTIR community for monitoring numerous tropospheric and stratospheric target gases.

Line parameters adopted in the spectral fitting process were taken from the HITRAN 2004 spectroscopic compilation (Rothman et al., 2005), including the August 2006 updates (e.g. Esposito et al., 2007). For CF_4, we selected a set of pseudo-lines whose intensities and temperature-dependent parameters were derived by one of us (G.C.T.) from a series of high resolution laboratory spectra recorded by Nemtchinov and Varanasi (2003) under pressure and temperature conditions typical of those encountered in the atmosphere.

The model atmosphere adopted above the 3.58 km Jungfraujoch altitude consists in a 39 layer scheme with progressively increasing thicknesses to reach 100 km altitude. The pressure-temperature profiles are those specifically computed for the ISSJ location on a daily noontime basis by the National Centers for Environmental Prediction (NCEP, Washington, DC; see http://www.ncep.noaa.gov).

While most of the strong Q- and R-branch features of the ν_3 band of CF_4 can be used for remote sensing retrievals from space between about 15 and 50 km altitude (see Fig. 18 in Zander et al., 1987), strong absorptions by H_2O, HDO, N_2O, CO_2, CH_4, and weaker ones, i.e. by HNO_3, $ClONO_2$ and H_2O isotopologues, combine to badly interfere with CF_4 features in low altitude spectra. Consideration of the relative importance of these interferences in typical solar recordings at the high-altitude, rather dry ISSJ site led us to adopt as "RUN 1" the spectral interval from 1284.73 to 1285.15 cm^{-1} displayed in Fig. 1, which encompasses 6 of the strongest R-branch features of the $CF_4\nu_3$ band. The relative absorptions of the targeted CF_4 as well as the major interfering gases computed for a typical spectrum observed on 1 April 2000, are displayed at the top of Frame A. The black curve (labeled "Sim." for simulation) corresponds to these combined absorptions. Its comparison to the selected spectrum (the green curve labeled "Obs.") results in the red residuals (observed minus calculated signals) displayed in Frame B, revealing poor fitting over the two middle CF_4 features, severely affected by H_2O and HDO interferences. For this reason, we excluded from our initial

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database all spectra whose water vapor content exceeded 8×10^{21} molec cm^{-2}, as well as those observed at solar zenith angles larger than 75 degrees to further minimize line-wing depression by the strong N_2O line centered at 1284.7 cm^{-1}. In addition to these limitations, and as illustrated in Fig. 1, we restricted the subsequent "RUN2" CF_4 interval to a composite window in which we excluded the two badly perturbed central CF_4 features (i.e. the spectral range from 1284.73 to 1285.15 cm^{-1}). Frame B shows that the RMS (root mean square) residuals reduced by about a factor 2 in RUN 2 as compared to RUN 1.

Notice that individual fitting, respectively over the left- and right part of RUN 2 returned CF_4 loadings that were, at most 3 % higher and 2 % lower than those derived over the full RUN 2. Such differences are considered as typical uncertainties for the pseudo-line parameters adopted here for CF_4 retrievals.

The a priori vertical concentration profile for the CF_4 target gas was set constant at 72 ppt throughout the atmosphere above ISSJ, consistent with values and associated uncertainties derived for the stratosphere (between 15 and 45 km altitude) from nearly 1400 solar occultations performed between February 2004 and mid-2012 in the 36.5 to 56.5° N latitude zone by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS; Bernath et al., 2005). As a result of the poor information content that characterizes the retrieved vertical distribution of CF_4 from individual ISSJ spectra, this constant a priori profile was simply scaled during the fitting procedure.

For all interfering molecules, averaged mixing ratio profiles based on WACCM (the Whole Atmosphere Community Climate Model; e.g. Chang et al., 2008) model predictions for the 1980–2020 period and the ISSJ station were used as a priori. To reliably account for the weak interfering absorption features by HNO_3 (see Frame A of Fig. 1), its concentration profile was pre-retrieved for each spectrum from a simultaneous fit to two dedicated spectral intervals (i.e., 867.05–870.00 and 872.25–874.00 cm^{-1}) commonly adopted within the frame of NDACC operations (Wolff et al., 2008). This pre-retrieved HNO_3 profile was then assumed in the consecutive fitting steps RUN 1 and RUN 2. During RUN 1, the vertical distributions of CF_4, CO_2, N_2O, HDO, H_2O, H_2O_2,

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$H_2^{17}O$ and $H_2^{18}O$ were independently scaled while in RUN 2, only the CF_4 profile was further adjusted. A S/N ratio of 500, commensurate with the noise level of most retained spectra, was adopted throughout the spectral fitting calculations. Inspection of an exo-atmospheric solar atlas by Farmer and Norton (1989) revealed only a very weak solar absorption feature at 1284.7666 cm^{-1}. It was neglected in the SFIT-2 retrievals, after verification that it had negligible influence on the CF_4 results.

After further exclusion of observations with S/N ratios lower than 300 and of few obvious high and low individual carbon tetrafluoride column outliers, the retained database upon which the following results and discussion are based includes 3034 individual CF_4 column measurements above ISSJ encompassing 1272 observational days.

Table 1 provides an error budget resulting from major instrumental and analytical uncertainties that may affect typical individual CF_4 column amounts above the site. They were evaluated according to referenced comments or perturbations to a representative subset of spectra. As is often the case when dealing with relatively "new anthropogenic" molecules (for which detailed fundamental spectroscopic laboratory studies are in progress and await validation), the largest systematic error in this work results from the CF_4 pseudo-line parameters (intensities and temperature dependences), which we set at ±6 % on the basis of evaluations discussed by Irion et al. (2002).

2.2 GCMS in situ measurements

The second original data set reported for the first time in this paper results from ground-based gas chromatography – mass spectrometry measurements conducted at ISSJ by Empa. The analyses are performed with a Medusa instrument described in detail by Miller et al. (2010), using 2 L of cryogenically trapped air alternated with measurements of a standard to calibrate the instrument. This leads to one air measurement every two hours. The CF_4 measurements at ISSJ began in 2008 but due to some instrumental difficulties, data are only reported here from 2010 onwards. Their precision is ∼ 0.4 %

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while the accuracy is estimated at 1–2 %. The measurements are based on the Scripps Institution of Oceanography (SIO) SIO-2005 calibration scale and are tightly linked into the AGAGE network.

3 Results and discussion

Figure 2 reproduces the daily mean vertical column abundances (expressed in numbers of CF_4 molecules per square cm; left vertical scale) derived above ISSJ between 1989 and 2012. They have been normalized to the mean local pressure monitored at the site during the past decades (i.e. 654 hPa) versus the daily surface pressure measured at noontime. The database reveals the relative sparseness and dispersion of the daily mean columns prior to about 1995, resulting from less frequent observations with the home-made instrument and their lower S / N ratios. However, as no statistically significant difference was observed between day-coincident CF_4 columns by both instruments, they have been merged in the post-1995 daily mean averages.

The right side scale of Fig. 2 reproduces the mean constant mixing ratio above ISSJ as returned by the SFIT-2 code on the basis of the physical P-T model atmosphere adopted for each day. The uncertainty on the conversion from left- to right scale is less than ±3 %. It should be noted that these mixing ratios correspond to moist values. However, correction factors to get dry air mole fractions would be very small, since only the driest observations were retained here (water vapor column of maximum 8×10^{21} molec cm^{-2}, for an air column of $\sim 1.4 \times 10^{25}$ molec cm^{-2} above ISSJ).

At first glance, two features emerge from Fig. 2, namely:

1. the large increase of the CF_4 column loading above ISSJ by 2.8×10^{14} molec cm^{-2} between 1989 and 2012, corresponding to +35 % when referenced to 1989. This increase is entirely of anthropogenic origin; it jumps to over 80 % when the "natural" background level of ~ 35 ppt, recently reported by Worton et al. (2007) and Mühle et al. (2010), is taken into account. As about one

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third of the atmospheric mass is located below the Jungfraujoch altitude (mean pressure = 654 hPa) and assuming that the very stable CF_4 gas is uniformly distributed through the atmosphere, its increase above ISSJ translates into a total column change above sea level equal to $+4.35 \times 10^{14}$ molec cm^{-2}, over 1989–2012. Globally, this has required a cumulated anthropogenic CF_4 emission at the ground totaling nearly 320 Gg over that time frame.

2. a significant slowing of the rate of CF_4 accumulation which we first evaluated by splitting the entire database into two subsets, i.e. before and after the 1 January 1998, respectively, the blue and green plus (+) symbols in Fig. 2. Application of the statistical bootstrap re-sampling method developed by Gardiner et al. (2008; a tool based on a Fourier series that allows calculation, at the 2σ confidence level, of the long-term linear component as well as the seasonal modulation of a given dataset), returned mean linear yearly increases above ISSJ of (1.38 ± 0.11) and $(0.97 \pm 0.02) \times 10^{13}$ molec cm^{-2}, respectively for the periods 1989–1997 and 1998–2012. Extrapolation of these increases down to sea level, as done in the previous paragraph, translates into yearly total column changes above sea level equal to $(2.14 \pm 0.17) \times 10^{13}$ and $(1.50 \pm 0.03) \times 10^{13}$ molec cm^{-2}. Globally, these changes require CF_4 emission rates equal to (15.8 ± 1.25) Gg yr^{-1} and (11.1 ± 0.2) Gg yr^{-1} for the above mentioned periods.

When taking into account a reasonable lag time of three years for ground-level emissions to uniformly mix in the free troposphere and in the stratosphere (e.g. Fabian et al., 1996; Waugh and Hall, 2002; Anderson et al., 2000; Stiller et al., 2008; Diallo et al., 2012), these derived CF_4 emission rates are commensurate with the 1986 to 2009 time averaged global emission estimates reported by Mühle et al. (2010, Table 6, i.e. 14.6 and 10.8 Gg yr^{-1}, for the 1986–1994 and 1995–2009 periods). A noticeable CF_4 seasonal cycle (close to 2 %, peak-to-peak amplitude) also deduced with the bootstrap re-sampling tool (Gardiner et al., 2008) is essentially ascribable to the seasonal variation of temperature versus pressure ratios in our adopted layered model atmosphere

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and to resulting impacts upon temperature- and pressure-dependent line intensities and half-widths.

In a second evaluation approach, the CF_4 database was "modeled" with both a second order fit and a 20 % smoothing function, respectively displayed in Fig. 2 by the black- and red curves. Discrete six-year time averaged trends determined from tangential derivatives to the black line at 1992.0, 1998.0, 2004.0 and 2010.0, return mean annual increases above ISSJ of, respectively (1.53 ± 0.41), (1.29 ± 0.11), (1.05 ± 0.07) and $(0.82 \pm 0.08) \times 10^{13}$ molec cm^{-2}, which translates into global emissions of (17.6 ± 4.7), (14.8 ± 1.25), (12.0 ± 0.8), and (9.4 ± 0.9) Gg yr^{-1}, respectively, for the periods 1989–1994, 1995–2000, 2001–2006, and 2007–2012.

These derived global CF_4 emissions are in line with the significant slowing in the CF_4 emission rates on the ground that began during the late 1980s, amplified during the early 1990s and leveled off subsequently, as synthesized by Mühle et al. (2010, Fig. 4). The mean global emission of 17.6 Gg yr^{-1} derived here for the 1989 to 1994 time interval is in good agreement with the mean increase rate of 18 Gg yr^{-1} derived by Zander et al. (1996) from upper stratospheric CF_4 measurements made in the Northern Hemisphere by the ATMOS FTIR instrument during the shuttle missions that occurred between 1985 and 1994 (Gunson et al., 1996).

The small but noticeable differences between the red- versus the black curve in Fig. 2 are indicative of slow temporal growth regime changes by up to + or −1.5 Gg yr^{-1} around the second order fit.

The conversion of our measured CF_4 column abundances above ISSJ into mean constant mixing ratios above the site (see Fig. 2), combined with the assumption that this molecule is uniformly mixed throughout the entire atmosphere allows some comparison with ground-level in situ- and FTIR solar occultation measurements from balloon- and space-based platforms. A few relevant examples, referring to data obtained at northern mid-latitudes, are displayed in Fig. 3, where the thick black line corresponds to the mixing ratios associated to the second order curve fitted in Fig. 2 to our daily mean CF_4 columns above ISSJ. The green curve reproduces an excerpt of

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the 1973 to 2010 assimilated monthly CF_4 mixing ratios for the northern extra-tropics (i.e., 30–90° N), based on AGAGE archived air samples and in situ measurements performed at Mace Head (Ireland) and at Trinidad Head (California, USA), and reported on the recent SIO-2005 calibration scale by Mühle et al. (2010), with a stated accuracy of ∼1 to 2 %. The green open circles show the monthly mean CF_4 mixing ratios at the ISSJ site measured by Empa within AGAGE, also reported on the SIO-2005 calibration scale and in excellent agreement with the other AGAGE data. The pink open triangles correspond to yearly averaged CF_4 mixing ratios derived by Khalil et al. (2003) from clean air samples collected at Cape Meares (45.5° N; OR-USA) and reported on the MPAE 86 calibration scale which has a stated uncertainty of ∼10 % (Fabian et al., 1996). The pink star corresponds to a CF_4 mixing ratio of 77.8 ± 0.6 ppt derived from one air sample collected in Tokyo (35.6° N) in August 2003, using a specific calibration approach based on the atmospheric ^{80}Kr abundance as reference; no calibration accuracy is reported (Aoki and Makide, 2005). The second order curve fitted to the pink triangles and the star is a typical representation of numerous ground-based monitoring efforts conducted in situ at northern mid-latitudes during the late 1970s onwards, as illustrated in Fig. 1 of Mühle et al. (2010). The latter showed that the accuracies of the calibration scales (namely MPAE 86 and UEA) adopted during these earlier activities, have reported uncertainties ranging by up to ±15 % and that related measurements can thus be reconciled with the recent, much more accurate ones based on the SIO-2005 calibration scale (1–2 %).

The filled orange circles represent stratospheric monthly mean CF_4 mixing ratios between 20 and 45 km altitude, derived from over 1400 solar occultation measurements (Version 3 products; Boone et al., 2013) in the 36.5 to 56.5 northern latitude zone between 2004 and 2012 with the satellite-embarked ACE-FTS instrument (Bernath et al., 2005). The four orange square symbols reproduce updated mean stratospheric CF_4 mixing ratios between ∼20 to 40 km altitude, derived from the 1985, 1992, 1993 and 1994 ATMOS missions (Version 3; Irion et al., 2002) as reported by Rinsland et al. (2006). Finally, the filled green triangles correspond to MkIV balloon measurements

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performed over 1990 to 2007, between 33 and 68° N latitude (e.g. Sen et al., 1996). Each triangle corresponds to a single flight and represents the average mixing ratio between 10 and 35 km altitude. The error bars associated to the ATMOS, MkIV and ACE data points correspond to the standard deviations of the means. As the space- and balloon-borne CF_4 retrievals were performed using the same cross-section parameters, not only for P-branch features but also for the strong Q-branch of the CF_4-ν_3 band, we assumed that their relative internal consistency was such that they could reasonably be interlinked with a 2nd order fitting, represented in Fig. 3 by the blue curve. It clearly shows the significant increase of CF_4 throughout the stratosphere over the past decades. The limited number of spectra recorded by ATMOS during the short pioneering US shuttle flights, as compared to the ongoing ACE-FTS mission, shows the advantage of regular, long-term monitoring approaches, which is also true for ground-based investigations. Table 2 provides mean annual mixing ratio increases determined by taking derivatives at 1990.0, 2000.0, and 2010.0 to the continuous curves displayed on Fig. 3.

The dashed horizontal line in Fig. 3 corresponds to the natural background level of ~ 35 ppt recently reported by Worton et al. (2007) and Mühle et al. (2010); it has been drawn here to better illustrate the relative anthropogenic contribution to the total CF_4 atmospheric burden which, since the turn into the 21st millennium, has overtaken the natural loading.

The differences between the various data sets displayed in Fig. 3 are obviously linked, at least partially, to atmospheric transport and can be ascribed to the fact that the instruments involved sound different layers of the atmosphere, namely the boundary layer for AGAGE and Empa as well as Cape Meares and Tokyo, the free troposphere and stratosphere for the FTIR observations, and the stratosphere only for the satellite and balloon data. Consequently, changes in the emissions of a long-lived gas on the ground will mix in the global troposphere within 1 to 2 yr, and propagate in the stratosphere by upwelling via the tropical pipe, reaching 20 km mid-latitudes within 3 to 5 yr (e.g. Elkins et al., 1996; Stiller et al., 2008). Examples of such time delays have

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also been reported by Anderson et al. (2000) who found that the inorganic chlorine and fluorine loadings in the stratosphere lag the related organic loadings at the ground by 4.5 to 5.5 yr. Inputs from the two-dimensional 12-box model of Mühle et al. (2010) indicate for 30–90° N a mean difference between the tropospheric and stratospheric mixing ratios of 2 ppt over the last decade, of more than 3 ppt in the early 1980s when the CF_4 emissions were stronger. In order to assess the adequacy (and possible bias) of having adopted a constant distribution in our column retrieval calculations and mixing ratio conversion, we built an a priori profile accounting for the time needed for CF_4 to propagate and mix in the stratosphere. Since the 12-box model only included a single stratospheric level, we based the construction of our a priori CF_4 distribution on a profile of mean age of stratospheric air parcels produced by Diallo et al. (2012), using ERA-Interim reanalyses and a Lagrangian model. Their findings have been confronted to satellite, aircraft and balloon observations, showing good agreement, including at northern mid-latitudes. For this region of the atmosphere of interest here, Figs. 2 and 6 of Diallo et al. (2012) provide profiles of mean age of air, with values close to 2 yr at 16 km, 3 yr at 18 km, 4 yr at 20 km and more than 6 yr above 25 km, i.e. showing a gradient of approximately 0.5 yr per km in the lowermost mid-latitude stratosphere, as quoted by Diallo et al. (2012). Assuming the CF_4 annual rate of change which prevailed over the last decade as derived by AGAGE, i.e. 0.7 ppt per year, our a priori profile was built such as to present a mixing ratio difference with the surface concentration of −1.4 ppt at 16 km, −2.1 ppt at 18 km, −2.8 ppt at 20 km, and so on, up to a constant difference of −4.5 ppt for altitudes above 25 km. All the 2009 observations were refitted with this non-constant vertical distribution, returning total columns on average 2.5 % higher. Conversion of these columns into corresponding surface mixing ratios resulted in values systematically higher by 3.7 %, or +2.9 ppt with respect to our standard run assuming a constant vertical distribution. Applying a vertical shift of +2.9 ppt to the FTIR function for 2009 brings it in very good agreement with the AGAGE and Empa time series, as indicated by the red segment matching the green curve and open circles in Fig. 3. This result gives good credibility on the absolute scale (1–2 %) provided

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by the SIO-2005 calibration standard as well as by the CF_4 spectroscopic parameters used in our analyses.

Nonetheless, one should keep in mind that the uncertainties associated to the various remote data sets presented in Fig. 3, namely 7 % for the FTIR dataset (see Table 1), 11 % for the revised ATMOS measurements and 7 % for the recent ACE-FTS data (Brown et al., 1996; Rinsland et al., 2006) have to be maintained as such, until further laboratory and related theoretical work narrow these uncertainties.

4 Summary and conclusions

Since the 1980s, the presence of carbon tetrafluoride (CF_4) in the Earth's atmosphere has attracted increasing attention for three reasons, namely: (i) its continued accumulation in our atmosphere, (ii) its extremely long lifetime, and (iii) its high global warming potential, 7390 times larger than that of CO_2, justifying priority recommendations by the Kyoto Protocol for CF_4 monitoring and regulation. In response to this recommendation, strongly endorsed by NDACC (Network for the Detection of Atmospheric Composition Change), we report the first spectrometric measurement from the ground of the atmospheric CF_4, and their comparison with recently reported ground-level in situ mixing ratios which have a quoted accuracy of 1 to 2 % (Mühle et al., 2010).

Owing to the location of the Jungfraujoch (3.58 km a.s.l.) above the polluted and wet boundary layer of the low troposphere, we have successfully established a special retrieval procedure that minimizes the perturbations by numerous interfering atmospheric gases, in particular the residual H_2O and HDO above the site (see Fig. 1), and determine with an accuracy of better than 7 % the loading of CF_4 throughout the free troposphere and the stratosphere (i.e. over two thirds of the total mass of the atmosphere) between 1989 and 2012. The spectrometric analysis of a subset of solar spectra recorded at ISSJ during this period (i.e. over 3000 spectra, encompassing 1272 days) has allowed, for the first time, the measurement of the long-term evolution of the CF_4 column abundance from ground-based remote FTIR observations.

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As illustrated in Fig. 2, the yearly mean CF_4 column increase above ISSJ was found equal to $(1.38 \pm 0.11) \times 10^{13}$ molec cm^{-2} between 1989 and 1997, and $(0.97 \pm 0.02) \times 10^{13}$ molec cm^{-2} from 1998 to 2012. Globally, these increases require 15.8 ± 1.3 and 11.1 ± 0.2 Gg yr^{-1}, respectively, resulting from anthropogenic CF_4 emissions at the ground in the earlier part of the record, primarily from the aluminum industry, and in the latter part also from the manufacturing of electronic devices. The significant slowing in the rate of increase is probably the result of efforts undertaken by the aluminum industry to comply with recommendations from the Kyoto Protocol. Considering our uncertainty, which is almost entirely due to the quality of the CF_4 spectroscopic parameters adopted here (±6 %), our findings are in good agreement with results derived by Mühle et al. (2010) based on selected ground level in situ measurements in the Northern Hemisphere from 1973 to 2008, and by new in situ GCMS measurements performed since 2010 by Empa at the Jungfraujoch. Moreover, we showed that the adoption of a vertical distribution for CF_4, accounting for the time needed for this very long-lived species to propagate and mix in the stratosphere, provided FTIR converted mixing ratios in very good agreement with the AGAGE data sets, giving good confidence in the absolute mixing ratios derived from the analyses involved here for both techniques.

We also note that the CF_4 FTIR time series is in excellent agreement (within 2 %) with solar occultation measurements made from satellites (ATMOS, ACE) and balloons (MkIV). This demonstrates the reliability of the spectral fitting procedures for retrieving CF_4 from the ground, in particular, the handling of the interfering H_2O lines (which are negligible in solar occultation retrievals above 10 km altitude).

During this study, we noticed that a synthetic CF_4 linelist produced by Boudon et al. (2011) was available in the "supplemental" section of the HITRAN 2008 compilation (Rothman et al., 2009). Running our entire dataset with these line-by-line parameters showed a reasonably good fit of the CF_4 line positions and contours. However, the retrieved column abundances were consistently and significantly larger than those derived with the pseudo-lines adopted here. This corroborates a conclusion by Boudon

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et al. (2011), stating that "the new linelist is still approximate concerning line intensities". We strongly encourage the continuation of such efforts aimed at improving the accuracy of line parameters for important atmospheric species.

Finally, it is worth mentioning that the new in situ local measurements of CF_4 performed by Empa at the Jungfraujoch within AGAGE open interesting possibilities for in-depth statistical intercomparison with the FTIR time series. This side-by-side, high-mountain operation is currently unique, worldwide, and is complementary in terms of techniques involved, vertical atmospheric coverage and, hopefully, long-term regular operation.

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

Error sources	Max. error (%)	Comments
	Random errors	
Spectra quality	4	Zero offset, S / N and instruments bias
H_2O and HDO a priori profiles	3	Changes by a factor 2 in a priori slope
Temperature/pressure profile	4	±4 K around NCEP noon profile; also column to mixing ratio conversion
Interfering gases H_2O, HDO and N_2O	3	Water vapor vertical distribution variability and wing slopes
Total	< 7	
	Systematic errors	
CF_4 spectroscopy	6	According to Irion et al. (2002)
H_2O and HDO spectroscopy	2	Assuming the HITRAN-04 uncertainties
CF_4 profile	3	Mixing time uncertainty
Forward model	1	Retrieval algorithm-related
ILS	2	±10 % misalignment and instruments bias
Total	< 7	

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Table 2. Annual rate of increase expressed in ppt yr^{-1} for atmospheric CF_4 computed for three reference times.

Data source	1990.0	2000.0	2010.0	Reference/Accuracy in %
Cape Meares + Tokyo	0.85	0.59	–	Khalil et al. (2003)/MPAE 86 (±10 %) Aoki and Makida (2005)
AGAGE + Empa	1.08 –	0.69 –	0.67 0.63	Mühle et al. (2010)/SIO-05 (±1–2 %) Empa/SIO-05 (±1–2 %)
ULg-FTIR	1.09	0.82	0.58	This work – see Table 1 (±7 %)
ATMOS + MkIV +ACE-FTS	1.40 –	0.95 –	– 0.60	Rinsland et al. (2006) (±11 %) This work (±7 %)

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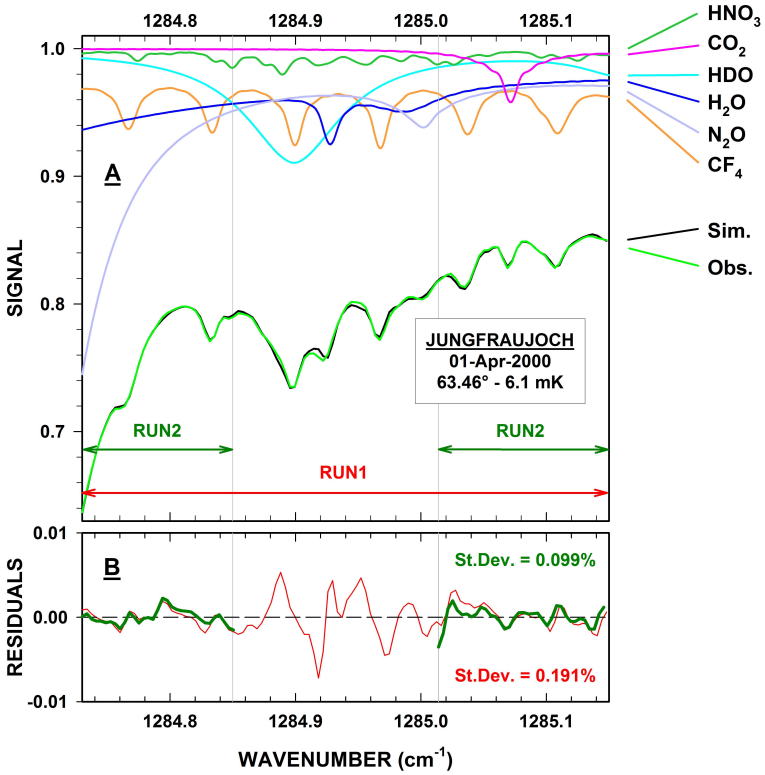

Fig. 1. Frame A displays the characteristic absorptions of CF_4 and the five most significant interfering gases in the micro-window selected for our CF_4 retrievals, computed for a typical observation at ISSJ on 1 April 2000. Their combination results in the simulation trace (in black, labeled "Sim.") which, compared to the actual observation (green curve, labeled "Obs.") leads to the red residuals in Frame B. Because of strong perturbations by the H_2O and HDO interferences, this initial "Run 1" was followed by a second composite "Run 2", with corresponding residuals displayed by the thick green trace in Frame B.

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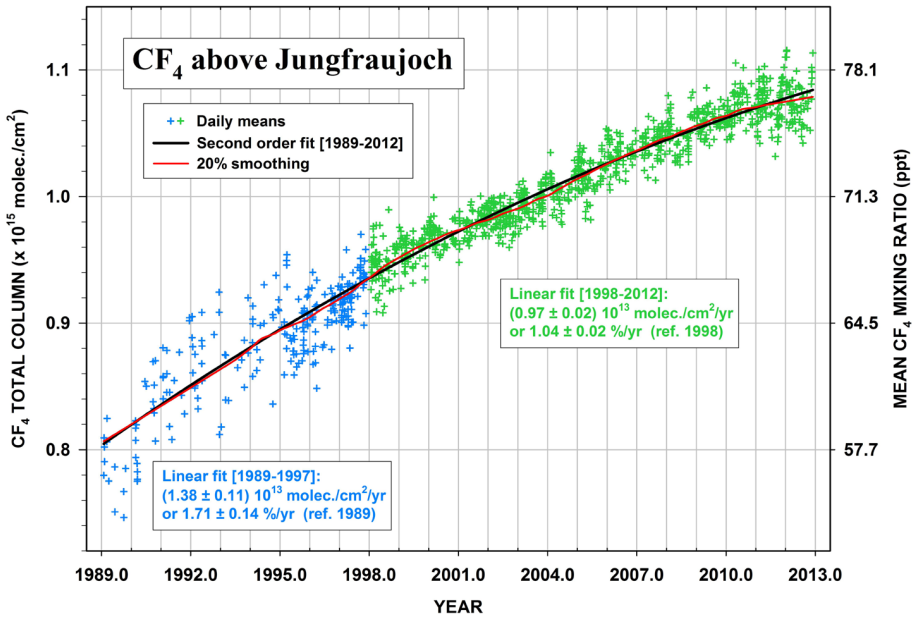

Fig. 2. FTIR time series of CF_4 daily mean vertical column abundances above the Jungfraujoch (expressed in numbers of CF_4 molecules per square cm), normalized to a mean local pressure of 654 hPa. The solid black and red curves correspond to a second order fit and a 20 % smoothing function to the data points, respectively. The right side scale allows conversion of our measured columns into mean constant mixing ratios above the site, expressed in ppt (parts per trillion).

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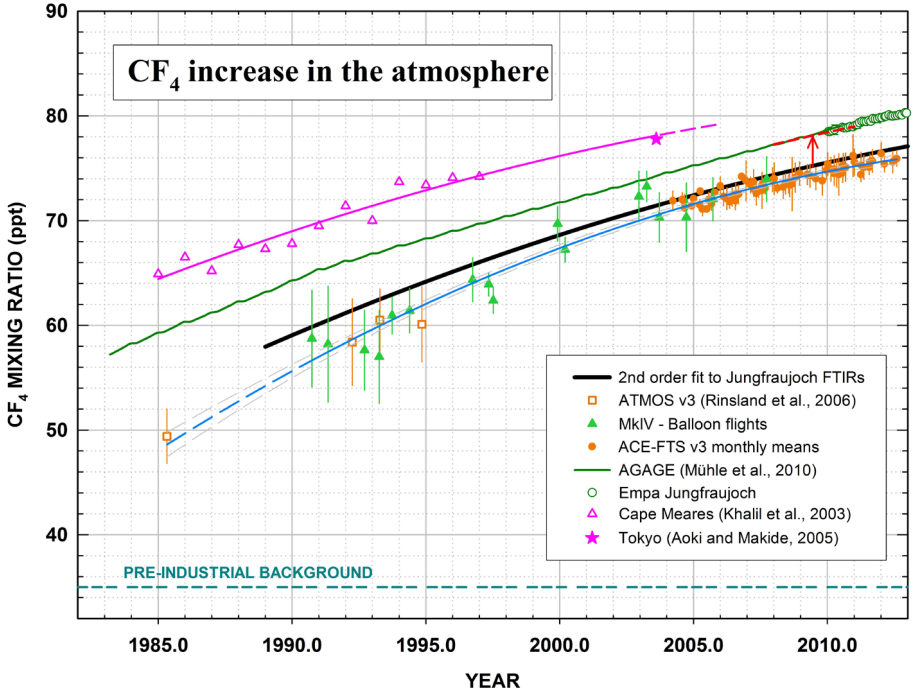

Fig. 3. Comparison between selected CF_4 mixing ratio time series and trends deduced from infrared remote-sensing and in situ surface measurements (see legend and text for their identification). It is important to note that all data sets can be reconciled in term of absolute concentration when accounting for the associated uncertainties affecting the retrieved quantities (calibration scales, line parameters) and time needed for a thorough mixing of CF_4 throughout the atmosphere. See text for details.

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