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Spectrometric monitoring of atmospheric carbon tetrafluoride (CF₄) 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 (CF₄) 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 R-branch of the strong ν_3 band of CF₄ centered at 1283 cm⁻¹, and two additional ones to optimally account for weak but overlapping HNO₃ interferences. The analysis reveals a steady accumulation of the very long-lived CF₄ 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 $(0.98 \pm 0.02) \times 10^{13}$ 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 CF₄ anthropogenic 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 northern mid-latitude

results obtained remotely from space and balloons as well as in situ at the ground, including new gas chromatography mass spectrometry measurements performed at the Jungfraujoch since 2010.

1 Introduction

Carbon tetrafluoride (CF₄) 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, 1979) have raised increasing attention and concern among the scientific community since the 1980s.

Its main anthropogenic source is primary aluminum production, during which CF₄ is released through “anode effect” episodes (e.g., Penkett et al., 1981; Khalil et al., 2003). Since the 1980s, non-negligible CF₄ emissions have also been released increasingly 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 CF₄ 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, CF₄ 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). Because of the absence of atmospheric sinks, CF₄ 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, for example, 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 CF₄ in the stratosphere was first reported by Goldman et al. (1979) who identified the strong ν_3 band of CF₄ 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, from subsequent MkIV FTIR balloon flights (e.g., Toon, 1991; Sen et al., 1996), and from the satellite ACE-FTS instrument (Atmospheric Chemistry Experiment Fourier Transform Spectrometer, e.g., Bernath et al., 2005; Brown et al., 2011).

Recent ground-level air sampling and in situ measurements of CF₄ 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 CF₄, attributed to efforts undertaken by the aluminum industry to limit its emissions during “anode effect” episodes (International (Primary) Aluminium Institute, 1996, 2009). However, significant uncertainties remain, amongst others due to the increase of Chinese aluminum production and insufficiently defined emission factors for Chinese smelters (International Aluminium Institute, 2013). Additionally, the magnitude and temporal evolution of CF₄ emissions from the semi-conductor industry remain very unclear, despite efforts by the World Semiconductor Council to reduce their emissions (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 CF₄ emissions which increased during the 1970s to reach their maximum during the early 1980s ($17.5 \pm 1 \text{ Gg yr}^{-1}$) 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 CF₄ 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 CF₄ in both hemispheres, reported by Mühle et al. (2010). Our concluding remarks include recommendations for improving the relative accuracies of spectroscopic CF₄ line parameters which currently remain estimated at $\pm 6\%$, as compared to the achieved 1–2% for the in situ data.

Since 1990, the University of Liège research activities 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 data sets

2.1 FTIR remote-sensing measurements and retrieval strategy

The long-term CF₄ 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 initial 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 CF₄ – 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 et al., 2004; Duchatelet et al., 2010), the other tool in use by the NDACC FTIR community for monitoring numerous tropospheric and stratospheric target gases, worldwide.

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 CF₄, 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 and high-S/N laboratory spectra recorded by Nemtchinov and Varanasi (2003) under pressure and temperature conditions typical of those encountered in the atmosphere. These pseudo-lines were also used for all CF₄ remote sensing measurements intercompared in Sect. 3 with our ISSJ findings.

The model atmosphere adopted above the 3.58 km Jungfraujoch altitude consists of 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 Q- and R-branch features of the ν_3 band of CF₄ 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 H₂O, HDO, N₂O, CO₂, CH₄, and weaker ones (i.e., by HNO₃, ClONO₂ and further H₂O isotopologues) combine to heavily interfere with CF₄ 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 CF₄ ν_3 band. Because of the poor fitting over the two middle CF₄ features, severely affected by H₂O and HDO interferences, we excluded from our initial 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 also minimize line-wing depression by the strong N₂O line centered at 1284.7 cm^{-1} . In addition and as illustrated in Fig. 1, we restricted the

subsequent “RUN2” to a composite window in which only the CF₄ profile was further adjusted. Frame B shows that the RMS (root mean square) residuals reduced by about a factor 2 in RUN 2 as compared to RUN 1. This RMS decrease was confirmed over the entire database, while the related CF₄ columns reduced by less than 0.7% on average.

The a priori vertical concentration profile for the CF₄ target gas was set constant at 72 ppt throughout the atmosphere above ISSJ, consistent with values and associated uncertainties derived for the stratosphere (in the 15 to 45 km altitude range) from nearly 1400 solar occultations performed between February 2004 and mid-2012 in the 36.5 to 56.5° N latitude zone by the ACE-FTS instrument. As there is poor vertical information content in the individual spectra, the constant a priori profile was simply scaled during our 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 HNO₃ (see Frame A of Fig. 1), its concentration profile was pre-retrieved for each spectrum from a simultaneous fit to two NDACC-dedicated spectral intervals (i.e., 867.05–870.00 and 872.25–874.00 cm^{-1} ; see Wolff et al., 2008). It was then assumed in the consecutive fitting steps RUN 1 and RUN 2. During RUN 1, the vertical distributions of CF₄, CO₂, N₂O, HDO, H₂O, H₂O₂, H₂¹⁷O and H₂¹⁸O were independently scaled while in RUN 2, only the CF₄ 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 CF₄ results.

After further exclusion of observations with S/N ratios lower than 300 and of high and low individual-carbon tetrafluoride-column outliers falling out of the $\pm 2.5\sigma$ confidence interval, the retained database upon which the results and discussion in Sect. 2.2 are based includes 3034 individual CF₄ 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 CF₄ 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 CF₄ pseudo-line parameters (intensities and temperature dependences), which we set at $\pm 6\%$ on the basis of evaluations discussed by

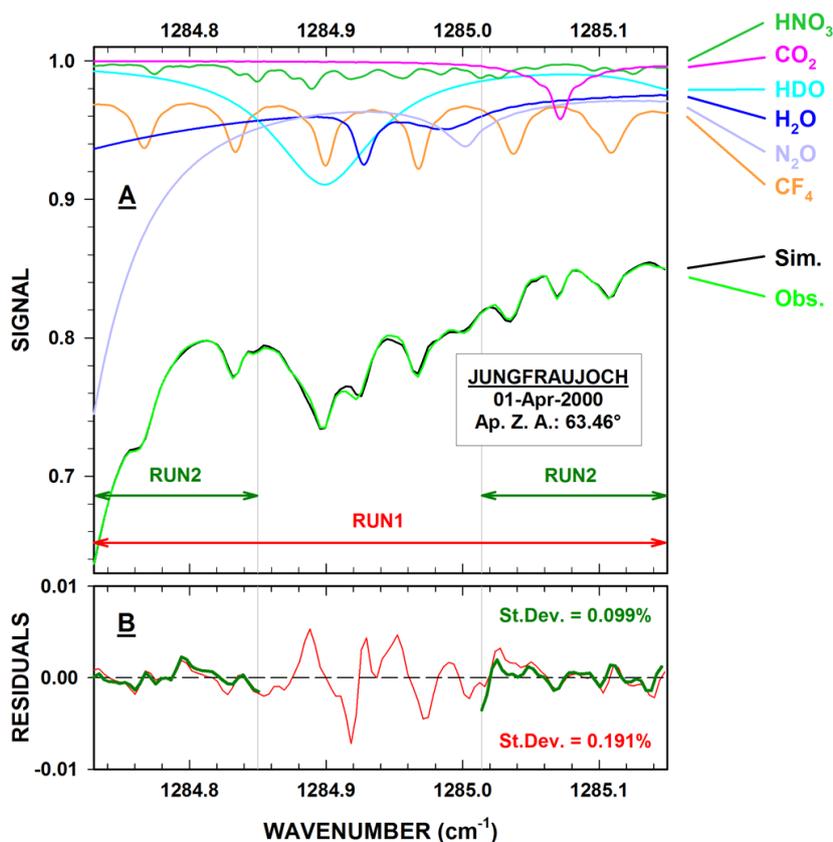


Fig. 1. Frame A displays the characteristic absorptions of CF₄ and the five most significant interfering gases in the “Run 1” micro-window selected for our CF₄ retrievals, computed for a typical ISSJ observation on 1 April 2000 (at 63.46° apparent solar zenith angle and 0.006 cm⁻¹ resolution). Their combination results in the black simulation trace (labeled “Sim.”) which, compared to the actual observation (green curve, labeled “Obs.”) leads to the red residuals (observed minus calculated signals) in Frame B. Because of strong perturbations by the H₂O 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.

Irion et al. (2002). A “quality-test” performed with a synthetic line-list covering the R-branch of the CF₄ ν_3 band, recently released by Boudon et al. (2011), will be evoked in Sect. 3.

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. (2008), 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 CF₄ measurements at ISSJ began in 2008 but due to some instrumental difficulties, data are only reported here from 2010 onwards. Their precision is $\sim 0.4\%$ 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 CF₄ 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 noon-time. 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 CF₄ 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 $\pm 3\%$. These mixing ratios correspond to moist air values. However, correction factors to

Table 1. Major sources of random and systematic errors on typical individual CF₄ total column retrievals above the Jungfraujoch.

| Error sources | Max. error (%) | Comments |
|--|----------------|--|
| Random errors | | |
| Spectra quality | 4 | Zero offset, S/N and instruments bias |
| H ₂ O and HDO a priori profiles | 3 | Changes by a factor 2 in a priori slope and local altitude variability |
| Temperature/pressure profile | 4 | ±4 K around NCEP noon profile; also column to mixing ratio conversion |
| Modeling of wing slopes | 2 | Water vapor and N ₂ O wing slopes affecting the local continuum |
| TOTAL | ~7 | |
| Systematic errors | | |
| CF ₄ spectroscopy | 6 | According to Irion et al. (2002) |
| H ₂ O 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 | |

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 major features emerge from Fig. 2, namely

- i. the large increase of the CF₄ 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 third of the atmospheric mass is located below the Jungfraujoch altitude (mean pressure = 654 hPa) and assuming that the very stable CF₄ 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, from 1989 to 2012. Globally, this has required a cumulated anthropogenic CF₄ emission at the ground totaling nearly 320 Gg over that time frame.
- ii. a significant slowing of the rate of CF₄ accumulation which we first evaluated by splitting the entire database into two subsets, that is, before and after 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 data set), returned mean linear yearly increases above ISSJ of $(1.38 \pm 0.11) \times 10^{13}$

and $(0.98 \pm 0.02) \times 10^{13}$ 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 CF₄ 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 CF₄ 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, respectively). A noticeable CF₄ 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 and to resulting impacts upon temperature- and pressure-dependent line intensities and half widths.

In a second evaluation approach, the CF₄ database was “modeled” with both a second order function and a nonparametric least-squares fit, respectively displayed in Fig. 2 by the black- and red curves. For the red curve, a local smoothing technique is applied, assuming a Gaussian weighting function and sampling 20 % of the data points at once. The actual bandwidth progressively considers all the measurements along the x axis (see Rinsland et al., 2003; and reference therein). Discrete six-year time averaged trends determined from tangential derivatives to the black line at 1992.0,

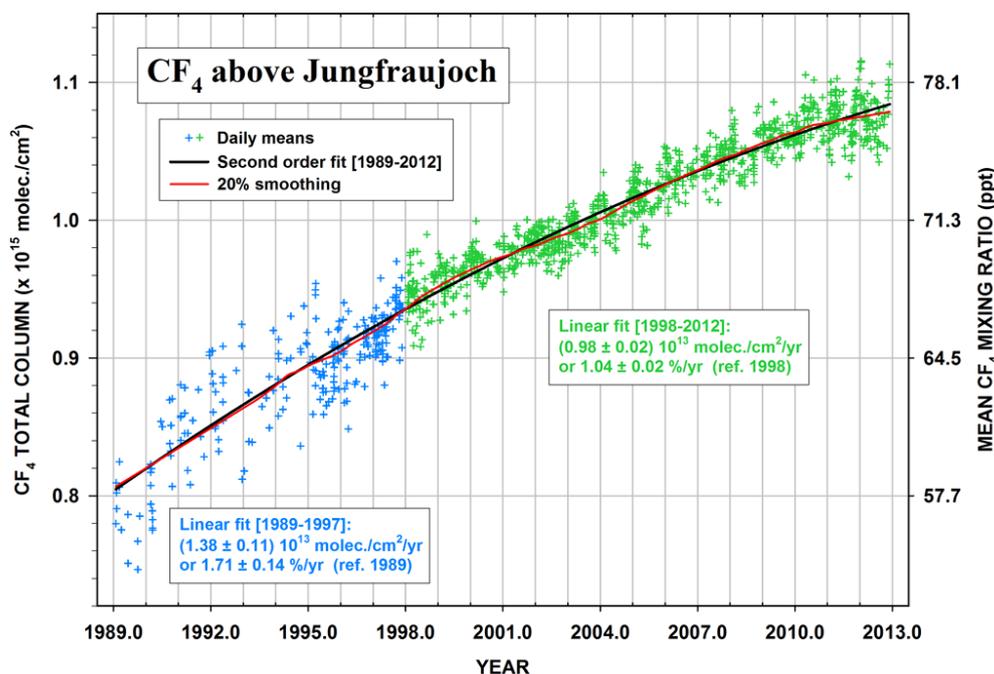


Fig. 2. FTIR time series of CF₄ daily mean vertical column abundances above the Jungfraujoch (expressed in numbers of CF₄ molecules per square cm), normalized to a mean local pressure of 654 hPa. The solid black and red curves correspond to a second order fit and a 20 % smoothing function to the data points, respectively. The coefficients of the second order black curve are (from the highest order to the independent term): -0.0194 , 78.72 and -79835 , in units of 10^{13} molec cm⁻². In the same units and rank, the coefficients of the linear regression are 1.385 , -2675 and 0.979 , -1862 , for the 1989–1997 (blue) and 1998–2012 (green) time periods, respectively. The right side scale corresponds to the conversion of our measured columns into mean constant mixing ratios above the site, expressed in ppt (parts per trillion).

1998.0, 2004.0 and 2010.0, and related global emissions are provided in Table 2. The latter are in line with the significant slowing in the CF₄ emission rates at 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 CF₄ 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- and black curves in Fig. 2 are indicative of slow temporal growth regime changes by up to $\pm 1.5 \text{ Gg yr}^{-1}$ around the second order fit.

A “quality-test” covering our entire database, performed by replacing the adopted CF₄ pseudo-lines by the synthetic line parameters of Boudon et al. (2011), as included in the “supplemental” section of the Hitran 2008 compilation (Rothman et al., 2009), led to the following appreciations: (i) the line positions are good; (ii) on average, the fitting residuals are $\sim 30\%$ higher; (iii) the retrieved CF₄ columns are consistently larger by $\sim 25\%$. We believe that this last observed difference may result from the fact that the Boudon

line list, currently restricted to the ν_3 R-branch, is only based on one high-resolution FTIR laboratory spectrum at 296 K and a low pressure of 0.17 torr, while the pseudo-lines were derived from a large set of spectra recorded at numerous typical pressure and temperature sets encountered throughout the atmosphere (Nemtchinov and Varanasi, 2003). However, another possible explanation is that this significant bias might also result from contributions, for example, by underlying hot bands of CF₄ not present in the Boudon line list (Rothman et al., 2009), while they are captured by cross-section measurements.

The conversion of our measured CF₄ column abundances into mean constant mixing ratios above ISSJ (see vertical scales in Fig. 2), assuming 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 black curve fitted in Fig. 2 to our daily mean CF₄ columns above the site. The green curve reproduces an excerpt of the 1973 to 2010 assimilated monthly CF₄ mixing ratios for the northern extra-tropics (i.e., 30–90° N), based on AGAGE archived air samples and in situ measurements

Table 2. Discrete six-year time averaged CF₄ trends based on tangential derivatives to the black line of Fig. 2, and corresponding emissions at 1992.0, 1998.0, 2004.0, and 2010.0.

| Data source | 1989–1994 | 1995–2000 | 2001–2006 | 2007–2012 |
|--|-------------|-------------|-------------|-------------|
| Columns above ISSJ in 10 ¹³ molec cm ⁻² yr ⁻¹ | 1.53 ± 0.41 | 1.29 ± 0.11 | 1.05 ± 0.07 | 0.82 ± 0.08 |
| Corresponding global emissions in Gg yr ⁻¹ | 17.6 ± 4.7 | 14.8 ± 1.25 | 12.0 ± 0.8 | 9.4 ± 0.9 |
| Emissions from in situ measurements in Gg yr ⁻¹ * | 15.1 ± 0.7 | 12.4 ± 0.6 | 11.0 ± 0.6 | 10.6 ± 0.4 |

* from Mühle et al. (2010), assuming a lag time of 3 yr for ground-level emissions to propagate in the free troposphere and stratosphere.

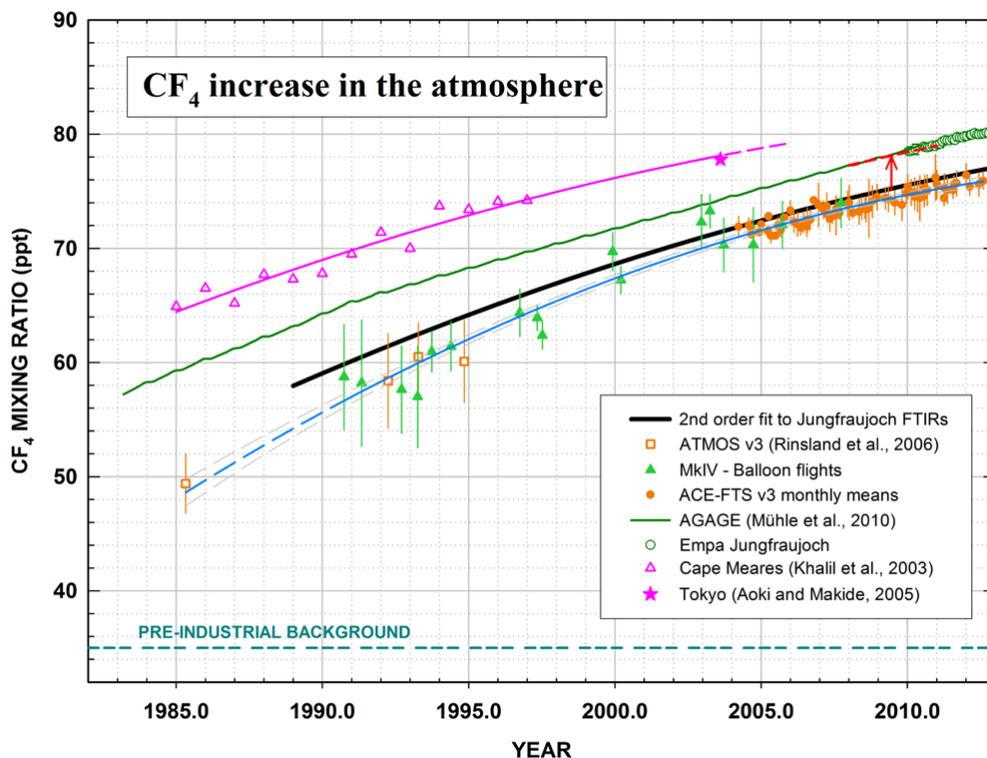


Fig. 3. Comparison between selected CF₄ mixing ratio time series and trends deduced from infrared remote-sensing and in situ surface measurements (see legend and text for their identification). The various data sets can all be reconciled in term of absolute concentration when accounting for the associated uncertainties affecting the retrieved quantities (calibration scales, line parameters) and time needed for a thorough mixing of CF₄ throughout the atmosphere. See text for details.

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 CF₄ 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 CF₄ 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 (Max Planck Institute for Aeronomy) calibration scale which has a stated uncertainty of ~ 10% (Fabian et al., 1996). The pink star corresponds to a CF₄ 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 ⁸⁰Kr 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 MPAE 86 and UEA (University of East Anglia) calibration scales 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 CF₄ mixing ratios between 20 and 45 km altitude,

Table 3. Annual rate of increase expressed in ppt yr⁻¹ for atmospheric CF₄ 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 %) |

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 CF₄ 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 the average mixing ratios between 10 and 35 km altitude derived from individual MkIV balloon flights performed over 1990 to 2007, between 33 and 68° N latitude (e.g., Sen et al., 1996). The error bars associated to the ATMOS, MkIV and ACE data points represent the standard deviations of the means. As all the space- and balloon-borne CF₄ retrievals were performed using the same cross-section parameters, not only for R-branch features but also for the strong Q-branch of the CF₄ ν_3 band, we assumed that they could reasonably be interlinked with a 2nd order fitting, represented in Fig. 3 by the blue curve. It clearly shows the significant but slowing increase of CF₄ 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, clearly shows the advantage of regular, long-term monitoring approaches, which is also true for ground-based investigations. Table 3 provides mean annual mixing ratio increases determined by taking derivatives at 1990.0, 2000.0, and 2010.0 to the continuous curves displayed in 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 CF₄ atmospheric burden which, since the turn into the 21st century, 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 our FTIR observations, and the stratosphere only for the satellite and balloon data. Consequently, changes in the emissions of a long-lived gas at 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 also been reported by Anderson et al. (2000) who found that the inorganic chlorine and fluorine loadings in the upper 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 and of more than 3 ppt in the early 1980s, when the CF₄ 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 CF₄ emitted at the ground 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 CF₄ 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 lower mid-latitude stratosphere). Assuming the CF₄ 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 observations of 2009 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 dashed red segment matching the green curve and open circles in Fig. 3. This result gives good credibility on the absolute scale (1–2 %) provided by the SIO-2005 calibration standard as well as by the CF₄ spectroscopic parameters used in our analyses.

Nonetheless, it remains that the uncertainties associated with the various CF₄ remote data sets presented in Fig. 3, namely 7 % for ISSJ (see Table 1), 11 % for ATMOS (Rinsland et al., 2006), 10 % for MkIV (Sen et al., 1996) and 7 % for the recent ACE-FTS data (Brown et al., 2011; Rinsland et al., 2006) have to be maintained as such, until further spectroscopic laboratory and related theoretical investigations narrow these uncertainties.

4 Summary and conclusions

Since the 1980s, the presence of carbon tetrafluoride (CF₄) 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 CO₂, justifying priority recommendations by the Kyoto Protocol for CF₄ monitoring and regulation. In response to these recommendations, strongly endorsed by the Network for the Detection of Atmospheric Composition Change, we have reported the first spectrometric measurement from the ground of the atmospheric CF₄, 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 established a special retrieval procedure that minimizes the perturbations by numerous interfering atmospheric gases, in particular the residual H₂O and HDO above the site (see Fig. 1), and successfully determined with an accuracy of $\pm 7\%$ the loading of CF₄ 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 CF₄ column abundance from ground-based remote FTIR observations.

As illustrated in Fig. 2, the yearly mean CF₄ column increase above ISSJ was found equal to $(1.38 \pm 0.11) \times 10^{13}$ molec cm⁻² between 1989 and 1997, and $(0.98 \pm 0.02) \times 10^{13}$ 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 CF₄ 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 CF₄ spectroscopic parameters adopted here ($\pm 6\%$), 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 CF₄, 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 CF₄ 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 CF₄ from the ground, in particular, the handling of the interfering H₂O lines (which are negligible in solar occultation retrievals above 10 km altitude).

During this study, we noticed that a synthetic CF₄ linelist produced by Boudon et al. (2011) was available in the formal HITRAN 2008 compilation (Rothman et al., 2009). Running our entire data set with these line-by-line parameters showed a reasonably good fit of the CF₄ line positions and contours. However, the retrieved column abundances were consistently larger by $\sim 25\%$ than those derived with the pseudo-lines adopted here. This corroborates a conclusion by Boudon et al. (2011), stating that “the new linelist is still approximate concerning line intensities”. We strongly encourage the continuation of such fundamental efforts aimed at improving the accuracy of line parameters for important atmospheric species.

Finally, we expect that the new in situ local measurements of CF₄ performed by Empa at the Jungfraujoch within AGAGE open interesting possibilities for in-depth statistical intercomparison with our 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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