

## Long-term stratospheric carbon tetrafluoride (CF<sub>4</sub>) increase inferred from 1985–2004 infrared space-based solar occultation measurements

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[1] The long-term stratospheric carbon tetrafluoride (CF<sub>4</sub>) increase has been determined from infrared high spectral resolution solar occultation Fourier transform spectrometer measurements between 3 and 50 hPa (~20 to 40 km altitude) and latitudes from 50°N to 50°S during 1985, 1992, 1993, 1994, and 2004. The 1985 to 1994 measurements were recorded from the ATMOS (Atmospheric Trace MOlecule Spectroscopy) instrument at 0.01 cm<sup>-1</sup> resolution and in 2004 by the Atmospheric Chemistry Experiment (ACE) instrument at 0.02 cm<sup>-1</sup> resolution. Stratospheric volume mixing ratios, inferred from a polynomial fit to averages from the time periods considered here, increased from 49.37 ± 2.60 pptv (10<sup>-12</sup> per unit volume) in 1985 to 58.38 ± 4.14 pptv in 1992, 60.46 ± 2.97 pptv in 1993, 60.11 ± 3.60 pptv in 1994 and to 70.45 ± 3.40 pptv in 2004. The stratospheric CF<sub>4</sub> mixing ratio has continued to increase but at a slower rate than in previous years, for example, (1.14 ± 0.68)% yr<sup>-1</sup> in 2004 as compared to (2.77 ± 0.47)% yr<sup>-1</sup> in 1985, 1 sigma. Correlations of CF<sub>4</sub> with N<sub>2</sub>O taking into account the increase of N<sub>2</sub>O with time also show the increase in the stratospheric CF<sub>4</sub> burden over the two decade measurement time span. Our space-based measurements show that the slowdown in the rate of CF<sub>4</sub> accumulation previously reported from surface measurements through 1997 has propagated to the stratosphere and is continuing.

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### 1. Introduction

[2] Carbon tetrafluoride (CF<sub>4</sub>) is a potent greenhouse gas 10,000 times more effective than CO<sub>2</sub> on a per molecule basis. As a result of its extremely long lifetime and with an increasing atmospheric abundance [e.g., Cicerone, 1979; Penkett *et al.*, 1981] the Kyoto Protocol which aims at preventing global warming from anthropogenic emissions of greenhouse gases has included CF<sub>4</sub> among key species to be regulated [*Intergovernmental Panel on Climate Change*,

2001]. Anthropogenic CF<sub>4</sub> emission is a byproduct of primary aluminum production and is released during brief interruptions in the aluminum electrolytic reduction process (“anode effect episodes”) [Khalil *et al.*, 2003]. Previous studies have shown there also are significant natural sources of CF<sub>4</sub> resulting in a background concentration of 40 pptv (1 pptv = 10<sup>-12</sup> per unit volume) in the troposphere [Harnisch and Eisenhauer, 1998]. An analysis of surface measurements in both hemispheres covering the last two decades indicates that the CF<sub>4</sub> increase rate has slowed due to major reductions in the emission rate per ton of aluminum produced, though the effect is partially offset by increased production and increasing use by the semiconductor industry [Khalil *et al.*, 2003]. We report here measurement of the long-term CF<sub>4</sub> stratospheric trend from an analysis of high spectral resolution infrared solar occultation spectra recorded in 1985, 1992, 1993, 1994, and 2004, and compare our results with previously reported surface and stratospheric findings.

### 2. Measurements

[3] The potential for high spectral resolution infrared solar occultation measurements from space was pioneered by the Atmospheric Trace MOlecule Spectroscopy (ATMOS) Fourier transform spectrometer (FTS) which flew successfully during 4 U.S. shuttle flights, Spacelab 3 from April 29–May 6, 1985, the Atmospheric Laboratory for Applications and Science (ATLAS) 1 mission from 24 March–3 April 1992, the ATLAS 2 mission from 8–16 April 1993, and the ATLAS 3 mission from 8–14 November 1994 [Gunson *et al.*, 1996]. Measurements at 0.01 cm<sup>-1</sup> resolution (50 cm maximum optical path difference) with a vertical resolution of 3–4 km were recorded with filters covering altogether 600–4800 cm<sup>-1</sup>. The main spectral interval for CF<sub>4</sub> measurements during the ATMOS missions was characterized by Zander *et al.* [1992, Table 1].

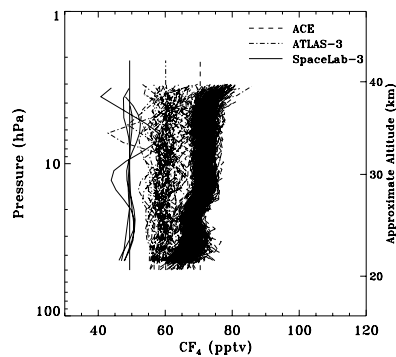
[4] Similar infrared FTS measurements are now being recorded by the Atmospheric Chemistry Experiment (ACE) launched on August 12, 2003 into a 74° inclined orbit at 650 km altitude [Bernath *et al.*, 2005]. The ACE FTS operates at 0.02 cm<sup>-1</sup> resolution (25 cm maximum optical path difference) and records occultations covering 750–4400 cm<sup>-1</sup> simultaneously. Similar to ATMOS, the ACE FTS is self-calibrating as low Sun spectra are divided by exoatmospheric spectra from the same occultation to remove solar lines and the variation of the instrumental response with wavenumber. Tropical to high latitude occultations below 150 km altitude are recorded with 3–4 km vertical resolution.

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**Figure 1.** CF<sub>4</sub> VMR profiles from version 3 ATMOS Spacelab 3 measurements during April–May 1985 and ATLAS 3 during November 1994 U.S. shuttle flights and ACE version 2.2 measurements recorded during 2004. Approximate altitudes are indicated on the right vertical axis. Vertical lines indicate the average VMR from each time period.

[5] We take advantage of the similar northern hemisphere stratospheric CF<sub>4</sub> latitudinal coverage during the ATMOS Spacelab 3 flights of April–May 1985 and November 1994, and also include measurements from ATLAS 1 and ATLAS 2, but avoid polar regions with strong descent. The ATMOS and ACE 2004 measurements are combined to provide coverage below 50° latitude in both hemispheres from the 1985, 1992, 1993, 1994, and 2004 time periods. All results are further compared with simultaneous measurements of the long-lived inert tracer N<sub>2</sub>O [Plumb and Ko, 1992] taking into account the increase rate of N<sub>2</sub>O as a function of time.

### 3. Analysis

[6] The intense  $\nu_3$  1282 cm<sup>-1</sup> band [Goldman *et al.* 1979] dominates CF<sub>4</sub> infrared absorption. Spectral parameters are based on temperature-dependent infrared absorption cross sections of Nemtchinov and Varanasi [2003] included in the HITRAN (High Resolution Transmission) 2004 compilation [Rothman *et al.*, 2005] as first updated in HITRAN 2002 [Rothman *et al.*, 2003]. ATMOS volume mixing ratios (VMRs) from version 3 [Irión *et al.*, 2002] have an estimated accuracy of 11% for CF<sub>4</sub>. Routine ACE FTS science measurements began in February 2004, and we adopt version 2.2 retrievals [Boone *et al.*, 2005], which provide VMRs with statistical uncertainties from an algorithm that retrieves temperature and VMR profiles from fits to multiple species in pre-selected microwindows over pre-specified altitude ranges. The two microwindows selected by ACE for their CF<sub>4</sub> retrievals are 1282.2–1284.2 cm<sup>-1</sup> for altitudes of 20–45 km and 1284.00–1285.00 cm<sup>-1</sup> for altitudes of 15–20 km. The spectral regions for CF<sub>4</sub> analysis include the Q branch and unresolved R branch manifolds. Major interferences in the target spectral range are CH<sub>4</sub> and N<sub>2</sub>O with minor interferences from CO<sub>2</sub>, H<sub>2</sub>O, HNO<sub>3</sub>, and ClONO<sub>2</sub> below 30 km [Zander *et al.*, 1996]. Absolute accuracies for ACE CF<sub>4</sub> have not been reported, but they are similar to those for ATMOS version 3 [Irión *et al.*, 2002].

[7] Figure 1 shows CF<sub>4</sub> VMRs from 50°S to 50°N latitude during 3 time periods. Approximate altitudes are

indicated on the right vertical axis. Objective criteria based on the precision have been used to exclude noisy occultations from the database. We retained 4 occultations from Spacelab 3, 25 from ATLAS 1, 12 from ATLAS 2, 47 from ATLAS 3, and 470 from ACE. Average VMR values between 3.0 and 50.0 hPa (~20–40 km) from the three time periods considered in Figure 1 are indicated by vertical lines. They provide strong evidence for a significant CF<sub>4</sub> increase from 1985 to 2004.

[8] The approach to quantify the CF<sub>4</sub> long-term trend is similar to the analysis of Spacelab 3 and ATLAS measurements. Averages of CF<sub>4</sub> measurements over the selected pressure range (3.0 to 50 hPa) from the time periods were fitted with the expression:

$$V = a_0 + a_1(t - t_0) + a_2(t - t_0)^2 \quad (1)$$

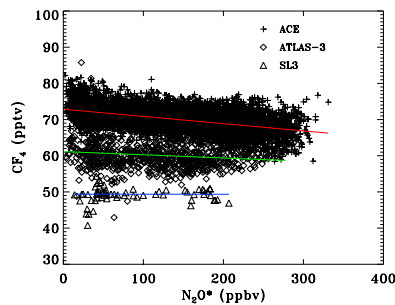
to determine the time dependence of  $V$  from fits to the 1985, 1992, 1993, 1994, and 2004 VMRs. In equation (1),  $t$  is time and  $t_0$  is the time of the measurements from the first ATMOS mission. The coefficients  $a_0$ ,  $a_1$ , and  $a_2$  and their statistical uncertainties were determined from a least-squares fit to each measurement set. Results for 1992 and 1993 are similar to those displayed in Figure 1.

[9] Based on the combined set from the 5 missions, we infer a best-fit (in pptv) of  $a_0 = 49.4866$  (1985 VMR),  $a_1 = 1.37458 \pm 0.231220$ , and  $a_2 = -0.0150236 \pm 0.0109374$ , one sigma. The best-fit corresponds to stratospheric VMR increases from  $(49.37 \pm 2.60)$  pptv and a rate of  $(2.77 \pm 0.47)$  % yr<sup>-1</sup> in 1985, to  $(58.38 \pm 4.14)$  pptv and a rate of  $(2.00 \pm 0.48)$  % yr<sup>-1</sup> in 1992,  $(60.46 \pm 2.97)$  pptv and a rate of  $(1.88 \pm 0.48)$  % yr<sup>-1</sup> in 1993,  $(60.11 \pm 3.60)$  pptv and a rate of  $(1.83 \pm 0.50)$  % yr<sup>-1</sup> in 1994, and  $(70.45 \pm 3.40)$  pptv and a rate of  $(1.14 \pm 0.68)$  % yr<sup>-1</sup> in 2004. The results were determined by taking derivatives at 1985, 1992, 1993, 1994, and 2004 and computing the trends at these time points. The combined set of average stratospheric CF<sub>4</sub> VMRs referenced to corresponding simultaneous N<sub>2</sub>O measurements from ATMOS and ACE indicate a CF<sub>4</sub> stratospheric increase by a factor of 1.43 over the two decade time period.

[10] We assumed a linear N<sub>2</sub>O VMR growth rate of 0.75 ppbv yr<sup>-1</sup> (1 ppbv = 10<sup>-9</sup> per volume) since 1977 based on measurements from Climate Monitoring and Diagnostics Laboratory (CMDL) surface stations [Elkins *et al.*, 2004]. The corrected N<sub>2</sub>O VMRs are noted hereafter by N<sub>2</sub>O\*. Figure 2 illustrates the combined sets of ATMOS Spacelab3 and ACE CF<sub>4</sub> measurements versus N<sub>2</sub>O\* with solid lines indicating best-fits for the three occultation sets. The long-term CF<sub>4</sub> trend derived from the VMRs vs. N<sub>2</sub>O\* best fits in Figure 2 is consistent with those calculated from average CF<sub>4</sub> VMRs vs. pressure and Equation 1 for the same time periods. The low slope is a consequence of the long stratospheric CF<sub>4</sub> lifetime [Plumb and Ko, 1992].

### 4. Comparison With Other Measurements and Reported Trends

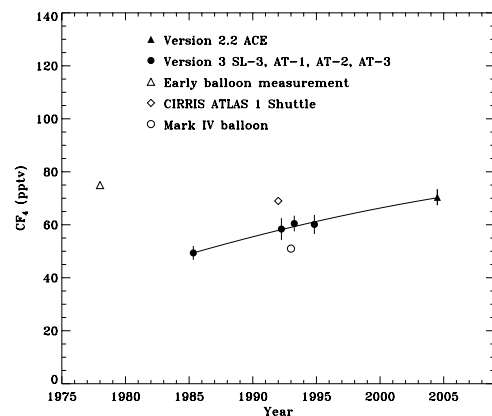
[11] Table 1 compares our results with surface and stratospheric measurements covering the last two decades. Tropospheric measurements are marked with an asterisk, and a 4-year constant tropospheric-stratospheric transport



**Figure 2.** Correlation diagram between CF<sub>4</sub> and N<sub>2</sub>O\* volume mixing ratios from ATMOS-ACE stratospheric occultations between 50°N and 50°S. Lines indicate best-fits to each subset.

time was added to approximate the delay with respect to mid-latitude stratospheric measurements. The few reported uncertainty (UNC) estimates are included. The combined set of ATMOS version 3 and ACE measurements and our best-fit with equation 1 to them are shown in Figure 3, which also displays the stratospheric measurements from Table 1. The scatter in Figure 3 suggests the impact of systematic errors. We next discuss evidence for inconsistencies in the infrared remote sensing stratospheric VMR data sets.

[12] The earliest infrared stratospheric remote sensing measurement from a October 1978 0.02 cm<sup>-1</sup> resolution solar occultation series yielded a preliminary CF<sub>4</sub> volume mixing ratio of 75 pptv at 25 km altitude based on a comparison of the integrated absorption of CF<sub>4</sub> in the atmospheric spectrum at that altitude with the integrated absorption measured in a room-temperature laboratory spectrum [Goldman *et al.*, 1979]. A nearly constant VMR of ~51 pptv above 20 km [Sen *et al.*, 1996] was retrieved from September 1993 northern midlatitude balloon solar occultation spectra assuming the ATMOS parameters [Brown *et al.*, 1987]. The spectral parameters were based on an incomplete prediction of the  $\nu_3$  band Q branch and P- and R-branch low  $J$  manifold parameters with relative strength measurements adjusted to be consistent with the Q branch parameters. The Cryogenic Infrared Radiance Instrumentation for Shuttle (CIRRIS-1A or C-1A) retrieval of 69 pptv [Zhou *et al.*, 1998] was based on limb emission



**Figure 3.** CF<sub>4</sub> volume mixing ratios vs. time based on the stratospheric measurements from Table 1. The solid curve shows the polynomial fit to the combined ATMOS version 3 and ACE version 2.2 observations with equation 1. SL3, AT1, AT2, and AT3 denote the ATMOS Spacelab 3, ATLAS 1, ATLAS 2, and ATLAS 3 missions, respectively. ACE measurements were derived from observations during 2004.

Fourier transform measurements recorded at 1.0 cm<sup>-1</sup> resolution during a April–May 1991 shuttle flight and parameters from the HITRAN 1992 database [Rothman *et al.*, 1992]. The offset of the stratospheric VMRs from the balloon flight solar spectra [Goldman *et al.*, 1979; Sen *et al.*, 1996], ATMOS version 2 solar spectra [Zander *et al.*, 1992, 1996], and the Cirris-1A 1991 emission measurements [Zhou *et al.*, 1998] result primarily from differences in the assumed intensity for the CF<sub>4</sub>  $\nu_3$  band and its dependence with temperature with respect to those assumed in both the ATMOS version 3 [Irion *et al.*, 2002] and the ACE measurements included in the present study. For example, an average CF<sub>4</sub> of 59 pptv for the 1985 VMR was reported from version 2 [Zander *et al.*, 1992] as compared to 49 pptv calculated here for the mean of 3.0–50 hPa volume mixing ratios from ATMOS version 3 [Irion *et al.*, 2002].

[13] Comparison of stratospheric with surface measurements requires consideration of the interhemispheric difference in surface sources and the time for transport of surface air to the stratosphere. The first factor is of minor importance as the interhemispheric difference in CF<sub>4</sub> volume

**Table 1.** Comparison of CF<sub>4</sub> Volume Mixing Ratio (VMR) Measurements (pptv) From ATMOS and ACE With Other Measurements<sup>a</sup>

Year	Data Source	VMR	UNC	Reference
1978	Stratospheric IR solar spectra	75		Goldman <i>et al.</i> [1979]
1982 <sup>b</sup>	Cape Meares gas chromatography	56	1	Khalil <i>et al.</i> [2003]
1985	ATMOS version 3 IR solar spectra	49	5	Irion <i>et al.</i> [2002]
1986 <sup>b</sup>	Stratospheric air corrected to surface level	62	3	Harnisch <i>et al.</i> [1996]
1992	ATMOS version 3 IR solar spectra	58	6	Irion <i>et al.</i> [2002]
1992	Cirris 1A ATLAS 1	69		Zhou <i>et al.</i> [1998]
1993	ATMOS version 3 IR solar spectra	60	6	Irion <i>et al.</i> [2002]
1993	Stratospheric balloon-borne solar spectra	51		Sen <i>et al.</i> [1996]
1994	ATMOS version 3 IR solar spectra	60	7	Irion <i>et al.</i> [2002]
1994 <sup>b</sup>	Cape Meares gas chromatography	68	0.4	Khalil <i>et al.</i> [2003]
1999 <sup>b</sup>	Stratospheric air corrected to surface level	75	3	Harnisch <i>et al.</i> [1996]
2001 <sup>b</sup>	Cape Meares gas chromatography	74	0.2	Khalil <i>et al.</i> [2003]
2004	ACE version 2.2 solar spectra	70	8	This study

<sup>a</sup>UNC = reported systematic error uncertainty (pptv). IR = infrared.

<sup>b</sup>Time includes the addition of 4 years to approximate the surface to stratosphere transport time.

mixing ratio is small, yielding a calculated northern/southern hemisphere ratio of  $(1.017 \pm 0.002)$ , close to the measured 1.019 during 1995–1998 [Khalil *et al.* [2003]. Annual averaged surface level CF<sub>4</sub> VMRs measured at Cape Meares, Oregon, U.S.A, from 1978 to 1997, and measurements recorded over shorter time periods at other sites have been reported recently [Khalil *et al.*, 2003]. The Cape Meares measurements show a CF<sub>4</sub> increase from 56.1 to 74.2 pptv. The measured and calculated surface trend indicated a slowdown in the CF<sub>4</sub> accumulation rate.

[14] Long-lived tracers such as CF<sub>4</sub> and SF<sub>6</sub> have been used to estimate atmospheric transport times [Harnisch *et al.*, 1996, 1999]. A CF<sub>4</sub> surface level increase from 62 to 75 pptv between 1982 and 1995 was inferred [Harnisch *et al.*, 1996]. However, the tropospheric to lower stratospheric transport time of 6 years at mid-latitudes is longer than assumed in other recent studies (e.g., Mahieu *et al.* [2004] assumed a 3.5 year delay). We adopted a tropospheric-stratospheric delay time of 4 years in Table 1 and Figure 3 as a compromise between estimates. As our trend relies only on the ATMOS version 3 [Irión *et al.*, 2002] and ACE stratospheric measurements, our results are not impacted by the uncertainty in the surface-stratosphere transport time. Nevertheless, the ATMOS-ACE time series is consistent with the Cape Meares surface time series assuming that the ATMOS version 3 CF<sub>4</sub> error estimate of 11% [Irión *et al.*, 2002] also applies to ACE.

## 5. Summary and Conclusions

[15] The long-term CF<sub>4</sub> stratospheric trend has been derived from ATMOS 1985, 1992, 1993, and 1994 version 3 and ACE 2004 version 2.2 measurements at 50°N–50°S latitude and 3.0–50 hPa (~20–40 km altitude). The low residual from the fit to the combined time set indicates their consistency and precision. We confirm the long CF<sub>4</sub> lifetime from correlations with simultaneous measurements of the long-lived tracer N<sub>2</sub>O correcting for its long-term increase. Our results have been compared with previous surface and stratospheric measurements over the last two decades, taking into account the transport time for surface air to reach the mid-latitude stratosphere. Our VMR time series shows that although stratospheric CF<sub>4</sub> is still rapidly increasing, the decline in the rate of accumulation (in pptv) reported from 1978–1997 surface measurements in both hemispheres [Khalil *et al.*, 2003] has propagated to the stratosphere and is continuing. The ATMOS-ACE set of mid-latitude stratospheric VMRs are based on the same spectroscopic parameters [Rothman *et al.*, 2005]. Furthermore, they agree with surface measurements considering the uncertainties in the time for transport of surface air to the mid-latitude stratosphere.

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