Long-term stratospheric carbon tetrafluoride (CF_4) increase inferred from 1985–2004 infrared space-based solar occultation measurements

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[1] The long-term stratospheric carbon tetrafluoride (CF_4) 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^{-1} resolution and in 2004 by the Atmospheric Chemistry Experiment (ACE) instrument at 0.02 cm^{-1} 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^{-12} 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_4 mixing ratio has continued to increase but at a slower rate than in previous years, for example, (1.14 ± 0.68)% yr^{-1} in 2004 as compared to (2.77 ± 0.47)% yr^{-1} in 1985, 1 sigma. Correlations of CF_4 with N_2O taking into account the increase of N_2O with time also show the increase in the stratospheric CF_4 burden over the two decade measurement time span. Our space-based measurements show that the slowdown in the rate of CF_4 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_4) is a potent greenhouse gas 10,000 times more effective than CO_2 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_4 among key species to be regulated [*Intergovernmental Panel on Climate Change*, 2001]. Anthropogenic CF_4 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_4 resulting in a background concentration of 40 pptv (1 pptv = 10^{-12} 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_4 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_4 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^{-1} resolution (50 cm maximum optical path difference) with a vertical resolution of 3–4 km were recorded with filters covering altogether 600–4800 cm^{-1}. The main spectral interval for CF_4 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^{-1} resolution (25 cm maximum optical path difference) and records occultations covering 750–4400 cm^{-1} 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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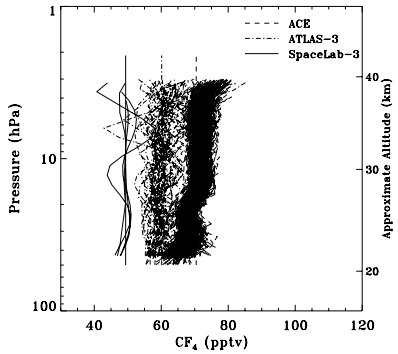

Figure 1. CF_4 VMR profiles from version 3 ATMOS Spacelab 3 measurements during April–May 1985 and ATLAS 3 during November 1994 U.S. shuttle flights and ACE version 2.2 measurements recorded during 2004. Approximate altitudes are indicated on the right vertical axis. Vertical lines indicate the average VMR from each time period.

[5] We take advantage of the similar northern hemisphere stratospheric CF_4 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_2O [*Plumb and Ko*, 1992] taking into account the increase rate of N_2O as a function of time.

3. Analysis

[6] The intense ν_3 1282 cm^{-1} band [*Goldman et al.* [1979] dominates CF_4 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 [*Irion et al.*, 2002] have an estimated accuracy of 11% for CF_4. 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 prespecified altitude ranges. The two microwindows selected by ACE for their CF_4 retrievals are 1282.2–1284.2 cm^{-1} for altitudes of 20–45 km and 1284.00–1285.00 cm^{-1} for altitudes of 15–20 km. The spectral regions for CF_4 analysis include the Q branch and unresolved R branch manifolds. Major interferences in the target spectral range are CH_4 and N_2O with minor interferences from CO_2, H_2O, HNO_3, and $ClONO_2$ below 30 km [*Zander et al.*, 1996]. Absolute accuracies for ACE CF_4 have not been reported, but they are similar to those for ATMOS version 3 [*Irion et al.*, 2002].

[7] Figure 1 shows CF_4 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_4 increase from 1985 to 2004.

[8] The approach to quantify the CF_4 long-term trend is similar to the analysis of Spacelab 3 and ATLAS measurements. Averages of CF_4 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 ± 0.231220, and a_2 = −0.0150236 ± 0.0109374, one sigma. The best-fit corresponds to stratospheric VMR increases from (49.37 ± 2.60) pptv and a rate of (2.77 ± 0.47) % yr^{-1} in 1985, to (58.38 ± 4.14) pptv and a rate of (2.00 ± 0.48) % yr^{-1} in 1992, (60.46 ± 2.97) pptv and a rate of (1.88 ± 0.48) % yr^{-1} in 1993, (60.11 ± 3.60) pptv and a rate of (1.83 ± 0.50) % yr^{-1} in 1994, and (70.45 ± 3.40) pptv and a rate of (1.14 ± 0.68) % yr^{-1} 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_4 VMRs referenced to corresponding simultaneous N_2O measurements from ATMOS and ACE indicate a CF_4 stratospheric increase by a factor of 1.43 over the two decade time period.

[10] We assumed a linear N_2O VMR growth rate of 0.75 ppbv yr^{-1} (1 ppbv = 10^{-9} per volume) since 1977 based on measurements from Climate Monitoring and Diagnostics Laboratory (CMDL) surface stations [*Elkins et al.*, 2004]. The corrected N_2O VMRs are noted hereafter by N_2O*. Figure 2 illustrates the combined sets of ATMOS Spacelab3 and ACE CF_4 measurements versus N_2O* with solid lines indicating best-fits for the three occultation sets. The long-term CF_4 trend derived from the VMRs vs. N_2O* best fits in Figure 2 is consistent with those calculated from average CF_4 VMRs vs. pressure and Equation 1 for the same time periods. The low slope is a consequence of the long stratospheric CF_4 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

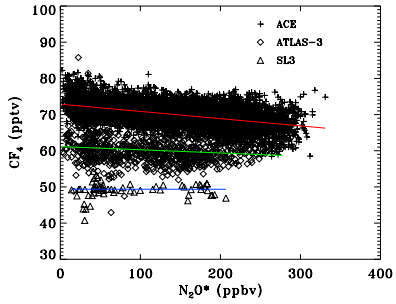

Figure 2. Correlation diagram between CF_4 and N_2O^* volume mixing ratios from ATMOS-ACE stratospheric occultations between 50°N and 50°S. Lines indicate best-fits to each subset.

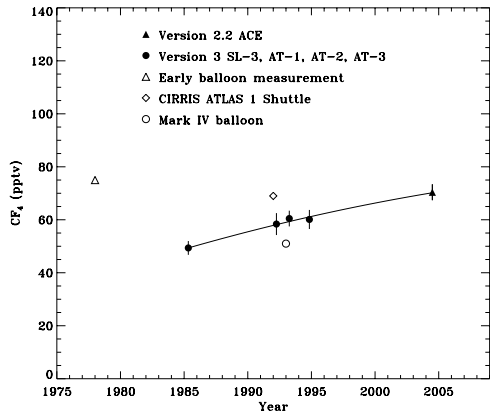

Figure 3. CF_4 volume mixing ratios vs. time based on the stratospheric measurements from Table 1. The solid curve shows the polynomial fit to the combined ATMOS version 3 and ACE version 2.2 observations with equation 1. SL3, AT1, AT2, and AT3 denote the ATMOS Spacelab 3, ATLAS 1, ATLAS 2, and ATLAS 3 missions, respectively. ACE measurements were derived from observations during 2004.

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^{-1} resolution solar occultation series yielded a preliminary CF_4 volume mixing ratio of 75 pptv at 25 km altitude based on a comparison of the integrated absorption of CF_4 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 ν_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 Fourier transform measurements recorded at 1.0 cm^{-1} 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_4 ν_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_4 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_4 volume

Table 1. Comparison of CF_4 Volume Mixing Ratio (VMR) Measurements (pptv) From ATMOS and ACE With Other Measurements[a]

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

[a]UNC = reported systematic error uncertainty (pptv). IR = infrared.
[b]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 ± 0.002), close to the measured 1.019 during 1995–1998 [*Khalil et al.* [2003]. Annual averaged surface level CF_4 VMRs measured at Cape Meares, Oregon, U.SA, 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_4 increase from 56.1 to 74.2 pptv. The measured and calculated surface trend indicated a slowdown in the CF_4 accumulation rate.

[14] Long-lived tracers such as CF_4 and SF_6 have been used to estimate atmospheric transport times [*Harnisch et al.*, 1996, 1999]. A CF_4 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 [*Irion 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_4 error estimate of 11% [*Irion et al.*, 2002] also applies to ACE.

5. Summary and Conclusions

[15] The long-term CF_4 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_4 lifetime from correlations with simultaneous measurements of the long-lived tracer N_2O 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_4 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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