INCREASE OF STRATOSPHERIC CAR11ON TETRAFLUORIDE (CF_4) BASED ON ATMOS OIWXVATIONS FROM SPACE

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Abstract Stratospheric volume mixing ratio profiles of carbon tetrafluoride, CF_4, obtained with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument during the ATLAS (Atmospheric Laboratory for Applications and Science) -3 mission of 1994 arc reported. Overall the profiles arc nearly constant over the altitude range 20 to 50 km, indicative of the very long lifetime of SF_6 in the atmosphere. In comparison to the stratospheric values of SF_6 inferred from the ATMOS/Spacelab 3 mission of 1985, the 1994 concentrations are consistent with an exponential increase of (1.6 ± 0.6) %/yr. This increase is discussed with regard to likely sources of CF_4 at the ground. Simultaneous measurements of N_20 and CF_4 have provided a means of constraining the atmospheric lifetime of CF_4 to well in excess of 1,500 years.

INTRODUCTION

Atmospheric carbon tetrafluoride (CF_4, also referred to as tetrafluoromethane, perfluoromethane, FC-14) is thought to have both natural and anthropogenic sources at the ground [i.e., Cicerone, 1979; Penkett et al., 1981; Fabian et al., 1987] but their identification and relative strengths have not been well established so far. Being a fully fluorinated organic compound, CF_4 is an inert tracer and has a very long lifetime recently estimated to lie between 25,000 and 50,000 years [Ravishankara et al., 1993]. Thus, it is expected to be uniformly mixed both geographically and vertically around the globe and to have a large "global warming potential" (GWP) due to its absorption characteristics in the infrared (IR) [Roehl et al., 1995].

Measurements of tropospheric CF_4 mixing ratios by Gassmann [1974] over Europe and by Rasmussen et al. [1979] and Penkett et al. [1981] in both hemispheres, indicated levels of tropospheric background concentrations in the (67 ± 10) pptv (parts per trillion by volume, or $\times 10^{-12}$ by volume) range, nearly the same worldwide. Stratospheric values have been measured locally by Goldman et al. (1979], i.e., 75 pptv at 25 km altitude, and over extended altitude ranges by Fabian and Goemer [1984] and by Fabian et al. [1987]. IR-remote measurements of the concentration versus altitude of CF_4 throughout the stratosphere and upper troposphere were reported by Zander et al. [1987, 1992], based on observations with the ATMOS (Atmospheric Trace Molecule Spectroscopy) instrument during the Spacelab-3 mission of 1985; they suggested that CF_4 has a nearly constant VMR ratio up to at least 50 km.

From the analysis of air samples collected at the South Pole in 1978-79 and 1984, Khalil and Rasmussen [1985] concluded that CF_4 accumulates in the Earth's atmosphere at a rate of about 2 % or 1.3 pptv/yr and suggested that the most likely anthropogenic source of CF_4 may be from releases associated with electrolytic aluminum and steel reduction processes (see also Penkett et al., 1981).

In this Letter, we report volume mixing ratio profiles of CF_4 retrieved from IR solar occultation observations with the ATMOS instrument during the 1994 ATLAS-3 mission and compare these with revised CF_4 profiles derived from the ATMOS/Spacelab-3 flight of 1985. We also report an estimate of the lifetime of CF_4 in the atmosphere, based on N_2O concentrations measured simultaneously.

DATA BASE AND ANALYSIS

The bulk of the results reported here have been derived from 0.01 cm^{-1} resolution infrared solar spectra obtained in the occultation mode with the ATMOS fast Fourier transform spectrometer [Farmer et al., 1987; Gunson et al., 1996] in low Earth orbit during the ATLAS-3 mission of November 3-12, 1994.

The spectra] region analyzed for CF_4 VMR profile retrievals extends from 1282.2 to 1285.2 cm^{-1}, and includes t he Q branch as well as a number of unresolved R branch manifolds of the very strong ν_3 band of the target molecule. Target and major interfering absorption by CH_4 and N_20 (also CO_2, H_20, HNO_3 and $ClONO_2$ below 30 km) arc accounted for in an iteration fit ting sequence using the spectroscopic parameters mint ained in the ATMOS line parameters compilation described by Brown et al. [1996]. In particular, the CF_4 VMRs reported here were derived with a realistic set of spectroscopic parameters used previously [Brown ct al., 1987; Zander et al., 1987] but scaled by a factor of 1.4 to account for new band strength estimates made by onc of us (A. G.) using the CF_4 ν_3 cross-sections reported by McDaniel et al. [1991]. Forward calculat ions and nonlinear least-squares spectral fittings were made with the ODS (Occultation Display Spectra) algorithm described by Norton and Rinsland [1991]. Details about data processing, retrieval procedure and ancillary input parameters arc discussed by Gunson et al. [1996].

All sunset occultations that occurred between 3 and 49°N and encompassed the ν_3 band of CF_4 have been analyzed consistently as part of the ATMOS - "Version 2" data set; they comprise 17 and 30 events observed with filters # 9 (600-2450 cm^{-1}) and # 12 (600-1400 cm^{-1}), respectively. This represents the largest single set of measurements which broadly overlaps the lat it udes (25 to 32°N) of the 1985 ATMOS observat ions [Zander et al., J 987]. Averages corresponding to subsets of spectra binned over specific latit udc and alt it udc ranges were also analyzed for consist ency of the results. Such averages improve signal-to-noise ratios of the resulting spectra, thus extending the range of detectability of the weak CF_4 features to higher alt it udes. Typical examples of sample spectra covering the interval fit ted for CF_4 retrievals have been reported in Figs. 17 and 18 of Zander et al. [1987], showing the weakness of the target absorption features in the upper st rat osphere and the ext ent of interfering absorpt ions below 30 km,

In addition to the northern sunset occultations mentioned before, the present analysis also evaluated CF_4 VMR profiles from the 14 filter # 9 and 27 filter # 12 sunrise occultations that occurred between 65 and 72° southern latitudes, both inside and outside the Antarctic vortex. CF_4 VMRS derived from ATMOS observat ions during the ATI .AS - 1 (03/24 to 04/02/92) and ATI .AS-2 (04/08 to 16, 1993) missions arc also reported for consistency.

RESULTS and DISCUSSION

FIGURE 1 reproduces VMR profiles of CF_4 derived from the ATMOS/ATLAS-3 occultations observed at northern latitudes, over the pressure range from about 1 to 50 mb (-50 to 20 km altitude). The increased scatter of the VMRs above 40 km is the result of the weakening of the target absorption features at high altitudes, while the curvature near the bottom of the profiles reflects a systematic effect resulting from the "Version-2" retrieval process and strong interfering absorption features. Local excursions of the data around the means are likely to result from propagation of errors associated with the onion-peeling retrieval method adopted here. One-sigma random errors with which individual profiles can be retrieved are discussed and documented by Gunson et al. [1996] and Abram et al. [1996]. Except where mentioned specifically, and because of the large number of occultations involved in this analysis, the standard deviations are representative of the precision assigned to the reported VMR profiles.

A characteristic feature that emerges from the CF_4 profiles displayed in Fig. 1 is their near-constant VMR in the stratosphere. The thick continuous and dotted vertical lines represent the average VMRs corresponding to the arithmetic means of the individual sunset profiles binned according to the ATMOS filter # 9 and filter # 12, respectively. These as well as similar averages derived from the ATLAS-3 sunrise occultations lie within the 71 to 76 pptv range (the filter # 9 results which extend only over the 20 to 40 km altitude range for quality reasons, are slightly larger (-2%) than those obtained from filter # 12) with their mean of 73,5 pptv having a standard deviation of 2.7 pptv and a precision of 3 pptv. This mean November 1994 VMR which applies at quite different latitudes around the Earth, is 17 % larger than the April-May 1985 mean CF_4 VMR of (63 ± 4) pptv retrieved from the 3 sunset occultations observed by ATMOS near 30°N during the April-May 1985 Spacelab-3 mission. The same analytical procedure was adopted for both 1985 and 1994 retrievals, in order to eliminate any biasing problem among all results reported in this Letter. The mean CF_4 volume mixing ratios retrieved here are summarized in **TABLE 1**.

The relative constancy of the VMR profiles versus altitude and latitude is indicative of the long lifetime of CF_4 in the atmosphere. This has already been suggested in earlier investigations [i.e., Cicerone, 1979] and was confirmed more recently by Ravishankara et al. [1993] and Morris et al. [1995] who re-evaluated all likely destruction mechanisms of CF_4 in the Earth's atmosphere and concluded that its lifetime may be as long as 25,000 to 50,000 years.

While constant VMR profiles (which would correspond to an infinite lifetime) were assumed in the above CF_4 trend evaluation, a more dct ailed binning versus height (at pressure levels consistent with the UARS pressure grid) reveals a weak decrease of the CF_4 VMRs with increasing altitude. This decrease derived from the large set of ATMOS/ATLAS-3 observat ions is statistically significant and can be used as an observational constraint on the atmospheric lifet imc of CF_4.

A first approach was based on correlations between simultaneous measurements of CF_4 and N_20, both being long-lived gases for which the steady state ratio of gradients can be assumed to be proportional to their lifetimes [Plumb and Ko, 1992]. **FIGURE 2 shows** the correlation plot derived from all sunset occultat ions binned in Fig. 1. The data used were rest ricted to the range of N_20 VMR values bet ween 3x10-8 and 2.5x1 0^{-7} ppv in order to avoid the extremes of the profiles where lack of sensitivity y (above 45 km) and uncertain yin the automat ic retrieval procedure (near and below 20 km) may degrade or bias the results. The slope of the straight line fitted to all data points in Fig. 2 is equal to 1.355×10^{-5}; assuming that N_20 has a lifetime of 120 years [WMO-Report Nr. 37, 1995], this slope translates into a "first order", minimum lifet imc of CF_4 equal to 1520 years. A similar evaluat ion performed by onc of us (S. S., privat c report) based on ATMOS/Spacelab 3 measurements of CF_4 [Zander et al., 1992] and N_2O [Gunson et al., 1990] led to a range of CF_4 lifetimes between 1500 and 5800 years.

However, a more detailed analysis must account for (i) the N_2O increase at a rate of 0.3 %/yr [WMO-Report Nr. 25, 1992; Zander et al., 1994], (ii) the CF_4 increase at a rate of 1.6 %/yr derived above and (iii) a troposphere-stratosphere mixing time of 4 years. One then finds a "second order", more realist ic CF_4 lifet imc in excess of 10,000 years (it should be noted that the CF_4 lifet imc evaluat ion is insensit ive to any systemat ic bias of the spectroscopic parameters used in the retrieval process, provided that such a bias applies similarly throughout the altitude range involved), Similar long lifet imcs for CF_4 have been suggested by von Clarman et al. [1995] and based on Mark] V-balloon measurements [B. Sen, private communication, 1995].

Concern may be raised about the above procedure's validity. Its applicability was assessed for various long-lived gases such as CCl_2F_2, CCl_3F, S1 'G, ... measured simultaneously with N_20 during the ATM(3S missions. For example, the application to CCl_2F_2 performed for 3 latitudinal zones, i.e., midlat it udes (49-35°N), subtropics (35-20°N) and tropics (20-3°N), all encompassed by sunset occultat ions during the Al'] .AS-3 mission, returned lifetimes of CCl_2F_2 for these zones equal to 121, 104 and 94 years, respectively. These values arc in excellent agreement with the mean global range of 102 to 111 years reported in WMO-Nr. 18 [1989] and WMO-Nr. 37 [1995] and reflect the latitudinal dependence of the lifetime, in particular its shorter value in the tropics where upward transport favours faster intrusion to altitudes where photodissociation proceeds.

How do the present results compare with other findings about atmospheric CF_4 ?

The atmospheric lifetime derived here points to a minimum value of 1500 years, ranging up to many thousands of years. The (1,6 ± **0.6)** %/yr rate of CF_4 increase throughout the stratosphere derived for the period separating the ATMOS mission of 1985 and 1994 is lower than (i) the 2 %/yr increase derived by Khalil and Rasmussen [1985] for the 65 pptv tropospheric background loading of CF_4 at the south pole between 1978 and 1984, and (ii) the 2.5 %/yr increase inferred from the CF_4 balloon VMR profiles reported by Fabian et al. [1987] when considering the 10 % decrease observed between 10 and 35 km altitude and invoking a mixing time of 4 years. All these trends arc, however, in agreement within their respective uncertainties.

CONCLUSIONS

Over the 9.5 year interval separating the ATMOS missions Spacclab-3 and ATLAS-3, the CF_4 increase was consistent with an exponential rate of (1.6 ± 0.6) %/yr, indicating that anthropogenic sources of CF_4 have made significant contributions to the present global loading. This is an important outcome, since the extremely long lifetime (minimum of 1500 years and very likely many thousand years) for carbon tetrafluoride in the atmosphere, leads to a G WP which is among the largest reported thus far, The upcoming ATMOS data processing will incorporate improvements in the spectroscopic data base [Brown et al., 1996; A. Goldman and P. Varanasi, private communications] and is expected to reduce the levels of uncertainty of the findings presented here. The need for spectroscopic parameters about "new", non traditional molecules whose interest has emerged during the last decade (this is certainly the case for CF_4) is stressed here; it should be performed in the laboratory under experimental spectral resolution conditions achieved with current state-of-the-art field instruments and span temperature and pressure ranges encountered throughout the entire lower and middle atmosphere.

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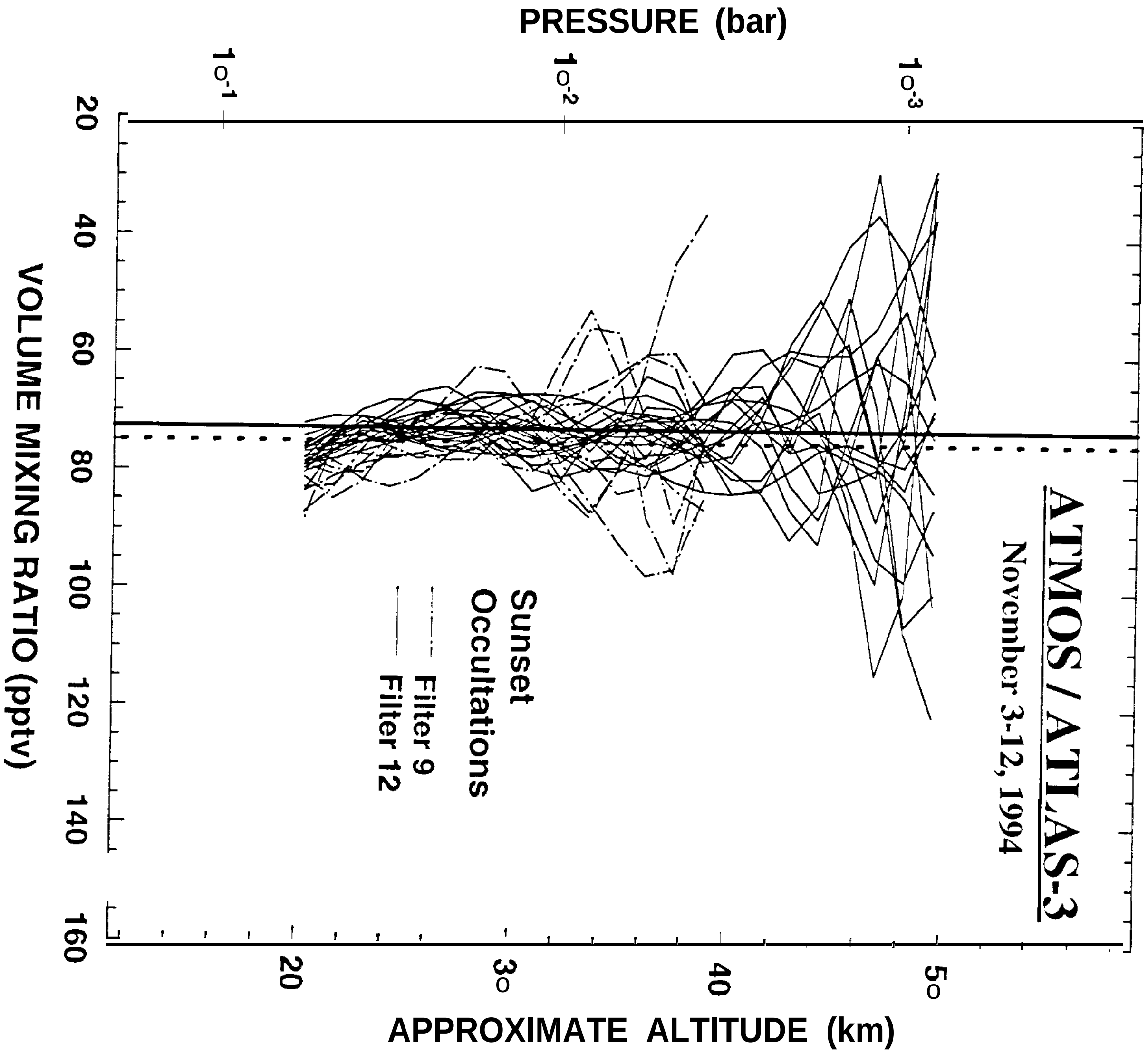
TABLE 1.- Summary of mean retrieved CF_4 VMRS over indicated pressure range

Mission	Nr. of occultations	Filter Nr.	Pressure range, mb	Retr. CF_4 pptv Mean	St.Dev.
s] .-3	1×SR	2	70-2	55.5	7.8
	3×SS	2	70-2	63.0	3.0
AT-1	14XSR	2,9	26-2	71.8	1.5
	13XSS	2,9	70-2	71.3	2.8
AT-2	19XSR	2,12	70-2	70.0	3.9
	13XSS	2,9,12	70-2	68.7	8.0
AT-3	41×SR	9,12	70-2	74.0	4.5
	47XSS	9,12	70-2	73.5	2.7

FIGURE CAPTIONS

FIGURE 1.- Series of CF_4 VMR profiles retrieved from sunset occult at ions that occurred bet ween 3 and 49°N during the ATMOS/ATLAS-3 mission of Nov. 3 to 12, 1994. The thick straight lines correspond to the mean constant VMR obtained from all profiles with filter # 9 (dotted line) and filter # 12 (continuous line).

FIGURE 2.- Correlation diagram of simultaneous CF_4 and N_20 VMR measurements for the sunset occultations reproduced in Fig. 1. The slope of the cent inuous straight line fitted to all data points has been used to evaluate the CF_4 lifetime throughout the stratosphere (for details, scc text),



PRESSURE (bar)
10^-1
10^-2
10^-3
ATMOS / ATLAS-3
November 3-12, 1994
Sunset
Occultations
Filter 9
Filter 12
VOLUME MIXING RATIO (pptv)
20
40
60
80
100
120
140
160
20
30
40
50
APPROXIMATE ALTITUDE (km)

11

FIGURE

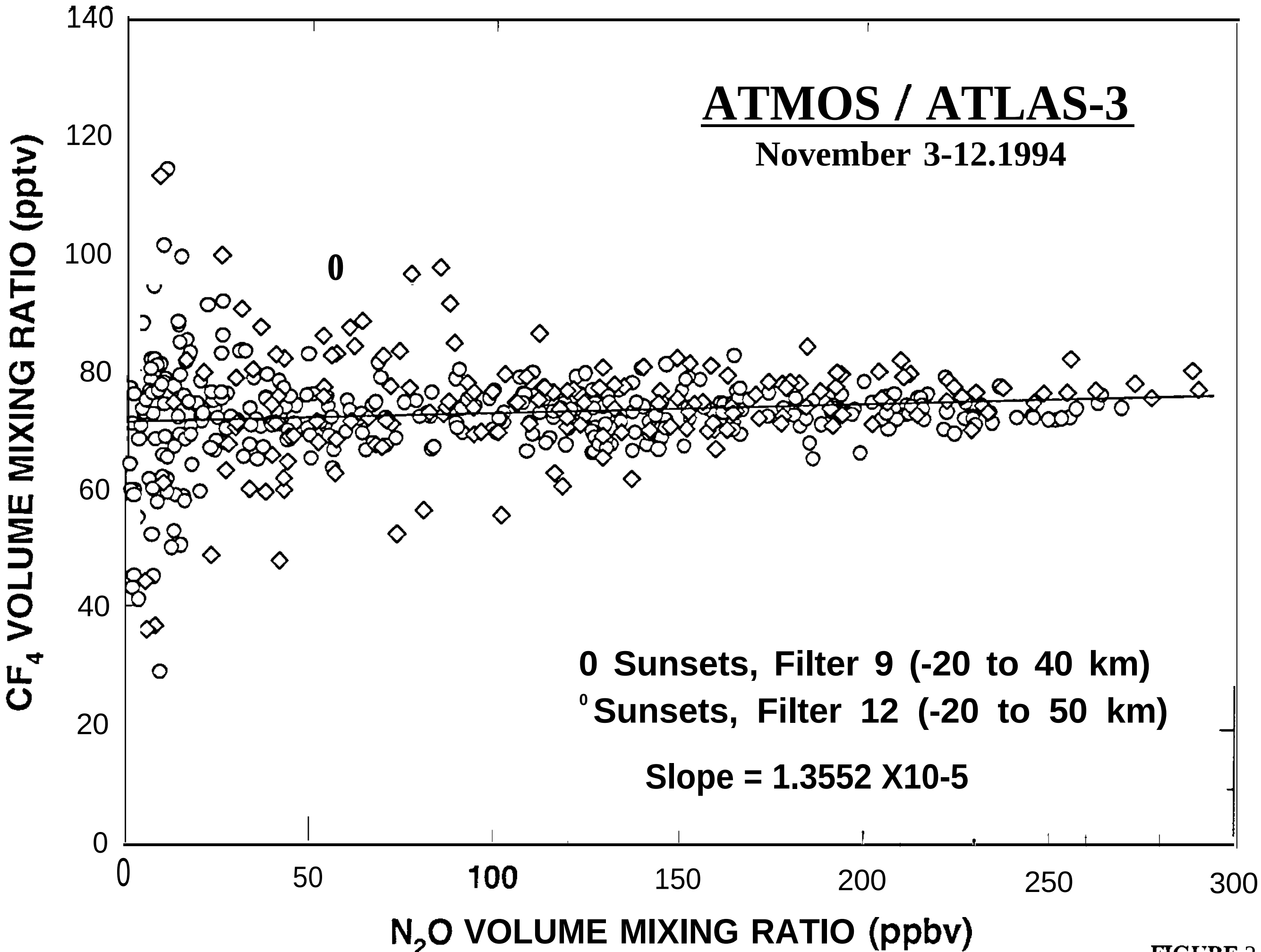

ATMOS / ATLAS-3
November 3-12.1994
0 Sunsets, Filter 9 (-20 to 40 km)
°Sunsets, Filter 12 (-20 to 50 km)
Slope = 1.3552 X10-5
CF_4 VOLUME MIXING RATIO (pptv)
N_2O VOLUME MIXING RATIO (ppbv)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300

FIGURE 2