Carbon tetrafluoride (CF_4) from MIPAS measurements

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Atmospheric Carbon Tetrafluoride (CF_4)

Carbon tetrafluoride (CF_4) is the most abundant perfluorocarbon in the Earth's atmosphere and one of the most potent greenhouse gases. It is estimated that a molecule of CF_4 is as effective as 10000 molecules of CO_2 for causing global warming [Khalil et al, 2003]. Because of this and its absorption characteristic in the infrared, emissions of CF_4 are restricted under the Kyoto-Protocol.

Two significant anthropogenic sources of CF_4 are known: the production of primary aluminum and the use of fluorocarbons in the semiconductor industry. In 1998, considerable concentrations of natural CF_4 were detected in a range of fluorite and granite sample [Harnisch and Eisenhauer, 1998]. At that time, it was estimated at 74 pptv of which about 40 pptv are from natural emissions, 33 pptv from aluminum manufacturing, and 1 pptv from the semiconductor industry.

The current atmospheric mixing ratio of CF_4 is about 70 pptv [Rinsland et al, 2006]. The measurements of Rinsland et al (2006), recorded from ATMOS and ACE , show that the growth rate of CF_4 has slowed in the recent years, for example, from (1.14 ± 0.68)% yr^{-1} in 2004 to (2.77 ± 0.47)% yr^{-1} in 1985, because during the past decade manmade emissions have been reduced considerably.

CF_4 has an extraordinarily long atmospheric lifetime (50 000 yr) and it is an extraordinarily stable compound with hardly any known destruction processes. Natural destruction processes seem to occur mostly in the mesosphere and thermosphere (above 60 km). A likely process that could destroy CF_4 molecules would be photolysis by solar Lyman-alpha radiation at 121.6 nm. Chemically very inert and long-lived atmospheric constituents, like CF_4, accumulate in the atmosphere, thus CF_4 is expected to be uniformly mixed both geographically and vertically around the globe.

CF_4 mixing ratios in the atmosphere are currently not monitored continuously. Recent trends of global emissions of CF_4 are therefore not known well enough to validate emission reductions reported by the industry. A better knowledge of the accumulation history of atmospheric CF_4 is also essential for its use as a conservative tracer of transport in the atmosphere.

MIPAS

MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) is a high resolution Fourier transform spectrometer flying on board ESA Envisat satellite. MIPAS measures infrared (685-2410 cm^{-1}) atmospheric limb emission spectra with a spectral resolution of 0.025 cm^{-1}. MIPAS observes sequences of spectra at different limb heights (6-68 km) to allow for the retrieval of species concentration profiles. The instrument has been operating at a reduced spectral resolution of 0.0625 cm^{-1} since January 2005, following problems with the interferometer slide mechanism. MIPAS spectra contain also information on CF_4. Here we present the feasibility of retrieving CF_4 and some preliminary results from MIPAS high resolution measurements.

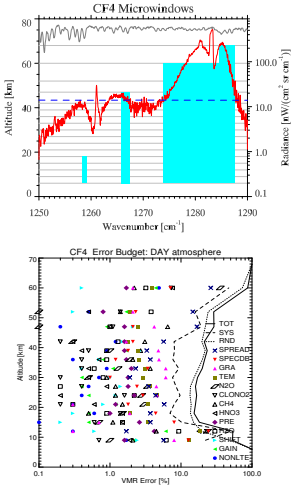

Figure 1: Microwindow location in spectral and altitude ranges (top panel) and error contributions to the total error for a single profile (bottom panel)

Microwindows for CF_4

Fig. 1 (top panel) shows the CF_4 contribution to the limb radiance at 12 km (red line) against the total limb radiance (grey line). The CF_4 signal exceeds the MIPAS NESR (blue dashed line) between 1274 and 1288 cm^{-1}, suggesting that the retrieval is feasible. This plot shows also the spectral coverage and the altitude ranges of the selected microwindows (shaded regions in light blue) chosen for CF_4 retrievals.

Error analysis for CF_4

The error analysis resulting from the microwindow selection is shown in the Fig.1 (bottom panel). The plot represents the total error (% VMR for a single profile) as a function of altitude. The total error (solid line) is given by random (dotted line) and the systematic (dashed line) profiles; the different symbols represent the major systematic components that affect the accuracy of the retrieval. Here, the accuracy for retrieving CF_4 is limited by the random error. Major interferences in the CF_4 spectral range are CH_4 and N_2O, which have been taken into account by jointly retrieve both species with CF_4.

Retrieval algorithm and Kalman Filter

The MORSE (MIPAS Orbital Retrieval using Sequential Estimation) retrieval algorithm uses an Optimal Estimation Technique with a-priori information to constrain the retrieval [Rodgers, 2000]. The retrieval is based on the use of selected spectral intervals (microwindows) containing the best information on the target parameters [Dudhia et al., 2002] and the line-by-line radiative transfer forward model used is the RFM (Reference Forward Model).

Since it is expected that there is little difference between the atmospheric CF_4 profiles between successive measurements, the previous MIPAS limb measurement (along the orbit track) can provide prior information about CF_4 at the current time. Here, we use the resulting profile (and associated covariance) as the starting point for the next retrieval (Kalman filter approach). In this way the prior information enters the retrieval only once and the random error on the final profile should be greatly reduced (approximately to a tenth of an individual retrieval).

Fig. 2 shows CF_4 zonal means (left panel) for the 22th of September 2003. A characteristic features that emerges from the CF_4 profiles in Fig. 2 is their near-constant VMR in stratosphere, between 300 and 3 mbar (approximately between 25 and 45 km). The relative constancy of the VMR profiles versus altitude and latitude is indicative of the long lifetime of CF_4 in atmosphere.

The right panel of Fig.2 shows the percentage Estimated Standard Deviation (ESD) relative to the CF_4 zonal means, obtained from the Kalman filter approach. The relative percentage error is of the order of or less than 10% altitude above 1 mbar surface.

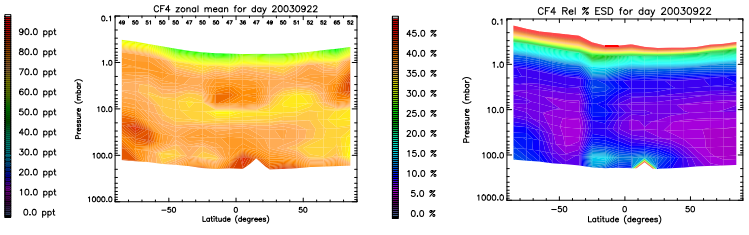

Figure 2: CF_4 zonal means [pptv] on the left panel and relative Estimated Standard Deviation [%] on the right panel, for 22nd September 2003.

Relationship between long-lived stratospheric constituents and lifetime calculation

For species with sufficiently long lifetime the relationship between their simultaneously measured mixing ratios is expected to be nearly linear and the slope of this relationship in the lower stratosphere can be related to the ratio of their atmospheric lifetimes. For two species whose sinks are purely stratospheric, which are in steady state and have a linear correlation in the lower stratosphere, then the ratio of their atmospheric lifetimes is: $\tau_1/\tau_2 \approx dV_2/dV_1 \cdot V_1/V_2$, if the mixing ratios V_1 and V_2 are evaluated in the very low stratosphere where V_1 and V_2 should be representative of tropospheric concentrations [Plumb and Ko, 1992].

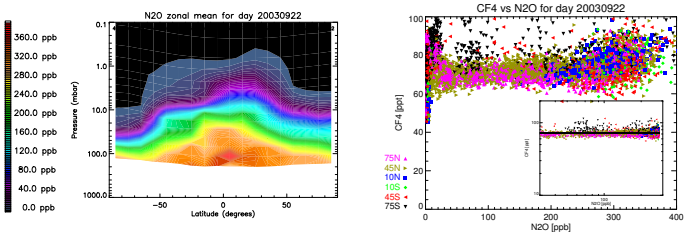

Figure 3: N_2O zonal means [ppbv] on the left panel and correlation diagram between CF_4 and N_2O on the right panel, for 22nd September 2003.

Correlation with N_2O

Correlations between simultaneous measurements of CF_4 and N_2O are used here to constrain the lower limit of the atmospheric lifetime of CF_4. Both CF_4 and N_2O are long lived gases for which the steady state ratio of gradients can be assumed to be proportional to their lifetimes.

Fig. 3 shows, on the left, the N_2O mixing ratios [ppbv], and on the right the CF_4 VMR against N_2O VMR. Each point corresponds to a matching geo-location. The mutual relationship is close to being linear for N_2O VMR grater than about 30 ppbv; this is indicative of very long lifetime of these constituents in the middle and lower stratosphere. The linear region is emphasized in Fig. 3 (in log scale in the small plot on the right panel), showing all points with N_2O VMR between 30 and 280 ppbv (approximately 25-45 km). Using a model calculated lifetime of 120 years for N_2O [Prather,1998], within this region the best fit line of the points gives an estimate of an atmospheric lifetime for CF_4 of 11143 ± 2080 years.

Since these two constituents have no chemical connection, this plot shows that the relationship between these tracers arises through transport effects. The degree of compactness of the relationship comes from the rapidity of the mixing (and the random noise on the measurements).

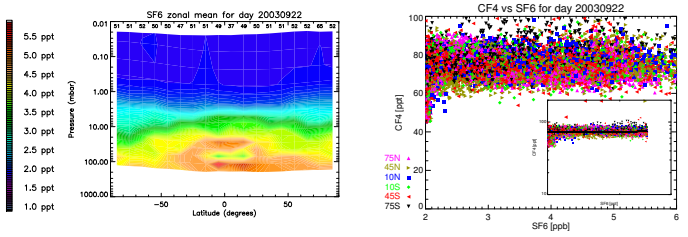

Figure 4: SF_6 zonal means [pptv] on the left panel and correlation diagram between CF_4 and SF_6 on the right panel, for 22nd September 2003.

Correlation with SF_6

Fig. 4 shows, on the left, the SF_6 mixing ratios [pptv], and on the right the CF_4 VMR against SF_6 VMR. Again, each point corresponds to a matching geo-location. SF_6 is almost non-existent above altitudes of around 30 km, as evident on the left panel. Because of this, the correlation diagram shows all point with SF_6 VMR grater than 2 pptv. Atmospheric lifetimes of SF_6 is about 1937 years and it has been calculated from stratospheric mixing ratio correlations with simultaneous measurements of N_2O and CFC-12 [Patra et al., 1997]. Using this estimated value of SF_6 lifetime and SF_6 VMR between 2 and 3.5 pptv (approximately between 25 and 45 km), we find an atmospheric lifetime for CF_4 of 11928 ± 735 years. The best fit line within this region is shown in Fig.4 (in log scale in the small plot on the right panel). The compactness of the relationship is less evident than the one with N_2O, due to the current SF_6 atmospheric concentrations less than five parts per trillion by volume.

Conclusions and further work

Here we have presented the feasibility of CF_4 profile retrievals from MIPAS measurements. Preliminary results from the 22nd of September 2003 show the relative constancy of CF_4 VMR profiles versus latitude and altitude, that is indicative of the long lifetime of CF_4 in atmosphere.

An atmospheric lifetime of about 11500 years has been calculated from stratospheric mixing ratio relationships of CF_4 with simultaneously observed distributions of N_2O and SF_6.

Lifetimes calculated from N_2O and SF_6 correlation diagram are in good agreement with each other.

Two years of MIPAS measurements and the new observation mode allow to provide information on seasonal VMRs and on long-term trends. We will look at MIPAS measurements up to 15 months apart for estimations of CF_4 trends to compare to the already existing ones [Risland et al., 2006].

The high degree of inertness coupled with longevity and very low natural emissions make CF_4 a good tracer for determining the age of stratospheric air [Harnisch et al, 1999 and Waugh and Hall, 2002]. In future we aim to calculate the age of air from CF_4 MIPAS measurements and compare these values with those derived from SF_6 MIPAS measurements [Burgess, 2005].

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