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TREND and LIFETIME of SULFUR HEXAFLUORIDE (SF_6) at MID-LATITUDES DEDUCED from ACE-FTS SOLAR OCCULTATION MEASUREMENTS

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1. INSTRUMENTATION AND OBSERVATIONAL DATABASE

- The ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) has been launched in August 2003 onboard the Canadian SCISAT satellite (Bernath et al., 2005). This instrument is still in operation to date, with no significant degradation of its performances. Since the beginning of routine operation in February 2004, it has recorded up to 15 sunrise and sunset occultations per day, with successive infrared solar spectra collected (within 2s) from 150 km altitude down to the cloud tops. The resulting vertical resolution is about 3-4 km, while a spectral resolution of 0.02 cm^{-1} is achieved in the broad 750-4400 cm^{-1} range. Signal-to-noise ratios of 200-300 are typically obtained in the spectral region of interest.

- Analyses of the ACE-FTS spectra are routinely performed at the University of Waterloo (Ontario, Canada), with an algorithm described by Boone et al. (2005). Numerous species are currently retrieved from the observations (see http://www.ace.uwaterloo.ca), among which sulfur hexafluoride (SF_6). The microwindow used to determine the vertical distributions of SF_6 encompasses its unresolved ν_3 band Q branch centered at 947.9 cm^{-1}. Critical interferences by CO_2 and H_2O adjacent lines have been accounted for. In the ACE-FTS version 3 (v3.0) used here, SF_6 volume mixing ratios (vmr) are retrieved in the 8 - 32 km altitude range.

- Here we analyzed all mid-latitude occultations (i.e. between 35 and 55°) in both hemispheres, from March 2004 onwards. TABLE 1 provides additional information about the data set under investigation. Altogether, about 1850 events were finally selected (after removal of a few profiles including obvious outliers). In FIGURE 1, we display all selected individual profiles for Northern and Southern mid-latitudes, in the left and right frame, respectively.

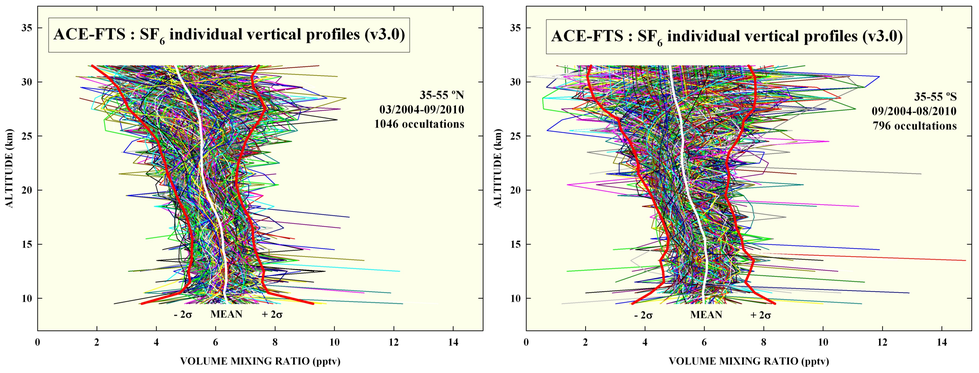

FIGURE 1. Individual vertical distributions of SF_6 retrieved from ACE-FTS solar occultation measurements performed at Northern and Southern mid-latitudes are shown on the left and right frame, respectively. In both cases, average profiles computed over the 2004-2010 time period are reproduced by the thick white lines while the thick red lines show the ±2-σ limits. It is clear that maximum measurement precision is achieved between about 12 and 22 km. Both mean profiles suggest a slight and regular decrease of SF_6 with altitude, from 6.4 to 4.65 pptv in the Northern hemisphere. In the Southern hemisphere, the UT/LS vmr is slightly lower (~6.0 pptv instead of 6.4 pptv). This results from the emission source distribution, with most of them located in the Northern hemisphere. In the following figures and analyses, only vmr values falling into the ±2-σ limits have been considered.

Latitude range	Time period	Number of selected occultations
35 – 55 °N	Mar-2004 – Sep-2010	1046 (1077)
35 – 55 °S	Sep-2004 – Aug-2010	796 (824)

TABLE 1. Information on the data set under investigation. The total numbers of occultations presently available from the ACE-FTS v3.0 data base and including SF_6 vertical profiles are indicated between parentheses. Only a few events were rejected.

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2. TREND DETERMINATION

- Relative standard deviations of about 10-12% are obtained in the 12-22 km altitude range (see FIGURE 1), where the better SF_6 measurement precision is achieved. Higher up, retrieved profiles show more noise. We have therefore selected all vmrs obtained below 22 km for the trend computation. To avoid the sampling of tropospheric air, we have further set the lower limit for the altitude range to 16 km.

- FIGURE 2 reproduces the daily mean vmr time series of SF_6 in the 16-22 km altitude range, in the Northern (green circles) and Southern (red circles) hemispheres, as deduced from the retained occultations . Error bars correspond to the standard deviations around the daily means. We further show linear fit to both data sets as thick lines. Narrow continuous lines show the 95% confidence interval associated to the linear regressions.

- FIGURE 2 reveals some interesting features: (i) trends in the Northern and Southern hemispheres are significant and commensurate, they amount to 0.20 ± 0.12 ppt/yr (2-σ); this value agrees well with in situ surface trends of 0.2 to 0.3 ppt/yr (WMO 2010; Figure 1 of Rigby et al, 2010), with growth rates of 0.23 pptv/yr derived from MIPAS 2002-2004 data (Stiller et al., 2008) and with an ACE-FTS tropical trend of 0.26 ppt/yr deduced by one of us [A.B.]; (ii) SF_6 build up in the Southern versus Northern hemisphere is delayed by 4 to 14 months, this results from emissions occurring mainly at Northern latitudes (see also Fig. 1).

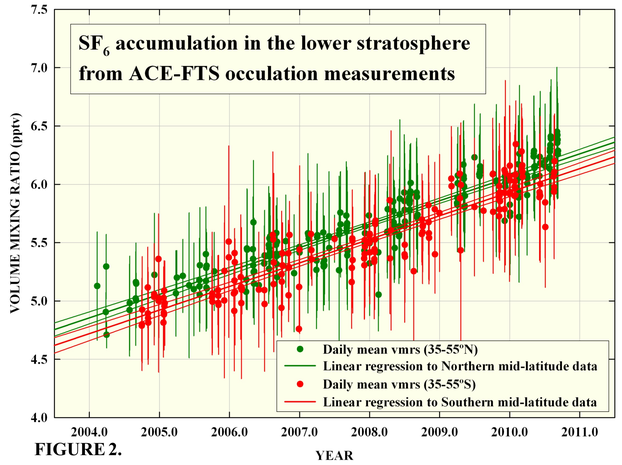

FIGURE 2.

BACKGROUND INFORMATION: SULFUR HEXAFLUORIDE IN THE EARTH'S ATMOSPHERE

- Sulfur hexafluoride has been detected in the Earth's atmosphere in the 1970s. Unlike carbon tetrafluoride (CF_4) which has natural sources, atmospheric SF_6 is believed to be entirely of anthropogenic origin. Its accumulation in our environment results primarily from its use in high-voltage electrical installations. Secondary contributions are related to magnesium and aluminum production as well as to the manufacturing of semiconductors (see e.g. Levin et al., 2010).

- SF_6 is one of the strongest greenhouse gases on a per molecule basis, with a global warming potential of 22800 (100-yr horizon). It is an extremely stable gas in the atmosphere, which results in a very long lifetime, with large uncertainties. The value adopted by IPCC is 3200 years, but some studies suggest shorter lifetimes, as low as 800 years (Morris et al., 1995). Because of these properties, SF_6 is among the species targeted by the Kyoto Protocol and its emissions are therefore inventoried and regulated.

- However, data sets deduced from in situ surface measurements indicate a strong and steady increase of SF_6 at rates up to 0.3 pptv/yr and a current global concentration of about 7 pptv. These observations are confirmed by the remote-sensing FTIR time series from the Jungfraujoch station (WMO 2010).

- Given all these characteristics, it is particularly important to monitor SF_6 and to accurately determine the evolution of its abundance, both in the troposphere and in the stratosphere.

3. SF_6 LIFETIME

- Plumb and Ko [1992] have shown that for sufficiently long-lived constituents, compact correlations between simultaneous measurements are obtained in the middle and lower stratosphere, at the global scale. Furthermore, for altitude regions where a linear correlation is found, the steady state ratio of the gradients of the two species versus altitude can be assumed to be proportional to their lifetimes [see also Zander et al., 1996, for an application to CF_4]. We used this relationship to evaluate the SF_6 lifetime, by considering concurrent nitrous oxide (N_2O) measurements.

- In FIGURE 3, we have reproduced all coincident measurements (18980) of N_2O and SF_6 available from the ACE-FTS version 3 data base, in the 9.5 to 31.5 km altitude range and between 35 and 55ºN. The vmr range observed for N_2O results from its progressive destruction by UV photons and O^1D, with increasing altitude. For SF_6, the vmr range extends from about 2 to 7.5 pptv, resulting from its progressive build up with time, but also from more noisy measurements at higher altitude.

- A linear regression to the N_2O-SF_6 data set reproduced on FIGURE 3 indicates a slope of (5.6 ± 0.1) $x10^{-6}$ (2-σ). A first order estimate of the SF_6 lifetime is obtained, considering equation 13 in Plumb and Ko [1992], the mean SF_6 and N_2O vmrs deduced here for the lower stratosphere and assuming a lifetime of 120 years for N_2O. This way, we determine a lower limit lifetime of ~400 years for SF_6. A more precise determination accounting for a SF_6 increase at a rate of 0.25 pptv/yr and for a delay of 4 years for tropospheric air to mix in the stratosphere leads to a lifetime of 2240 years. These findings are confirmed when considering the corresponding data set for 35-55ºS, or when looking at individual yearly subsets.

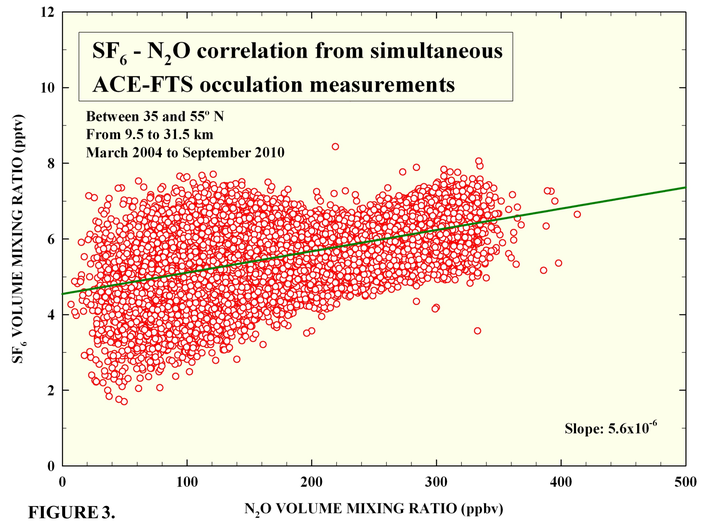

FIGURE 3.

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