Determination of COF_2 vertical distributions above Jungfraujoch by FTIR and multi-spectra fitting

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1. INTRODUCTION

The major sources of fluorine in the stratosphere are CFC-11 and CFC-12. Photolysis of these compounds leads to release of chlorine atoms, while the fluorine is, in a first step, present in the form of carbonyl compounds like COClF and COF_2. Their further photolysis liberates fluorine atoms, which are quickly converted to HF. Given its long life time, COF_2 is the second stratospheric fluorine reservoir [1].

The first COF_2 vertical distributions were derived from occultation measurements performed by the ATMOS instrument during the SPACELAB-3 Space Shuttle mission in 1985 [2]. The Canadian FTIR spectrometer ACE-FTS, onboard the SCISAT-1 satellite, is the first instrument since the last ATMOS flight in 1994, to record COF_2 vertical profiles from space. All these observations show that, at mean latitudes, COF_2 concentration is maximum between 30 and 35 km.

Several COF_2 IR absorption lines located either in the so-called InSb (2-5.5 μm) and MCT (7-14 μm) spectral ranges can be used to determine its total column from ground-based FTIR observations. In this context, several studies concerning the evolution of COF_2 total column above various stations were published during the nineties (for example, see [3], [4], [5] and [6]). At this time, no study concerning the inversion of COF_2 vertical distributions from ground-based FTIR spectra has been published. This contribution deals with the feasability of such inversions.

2. WORK STRATEGY

Table 1 presents the two sets of microwindows (in the InSb and MCT ranges, respectively) we have selected to retrieve COF_2 vertical distributions from high resolution FTIR spectra recorded at the International Scientific Station of the Jungfraujoch (ISSJ - 46.5°N, 8.0°E, 3580m asl). For each of these sets, such inversions have been performed using the SFIT-2 v3.91 algorithm and the HITRAN 2004 spectroscopic line parameters database. During the retrievals, all microwindows of each sets are fitted simultaneously. To increase the information content (see also relevant pannel), we also proceed to multi spectra retrievals : it consists of combining several FTIR spectra, recorded during the same day.

Between 15 and 37 km, the adopted a priori COF_2 profile is a zonal mean (for the latitudinal band [41-51]°N) of the more than 300 occultations recorded by the Canadian satellite ACE-FTS between February 2004 and September 2005. Below 15 km, a realistic decrease has been constructed to reach low COF_2 VMR values of about 1×10^{-13} at the altitude site. Above 37 km, we have kept the a priori COF_2 profile used by the ACE-FTS instrument for its own retrievals. The a priori covariance matrix S_a has been deriving from the same set of ACE-FTS measurements used for the construction of the a priori COF_2 profile. We have also modelized a gaussian inter-layer correlation of 2km, deduced from the 3D VMR-altitude correlation matrix, as seen by the ACE-FTS instrument.

Range (cm^{-1})	Interfering species	DOFS ($_1$)
InSb range		
1936.15-1936.34	O_3, CO_2, H_2O, solar lines	0.53 (0.49)
1951.89-1952.05	O_3, H_2O, solar lines	0.58 (0.53)
1952.62-1952.78	O_3, CO_2, solar lines	0.60 (0.54)
MW		0.94 (0.53)
$MW+MS_{[3obs]}$		1.24 (0.92)
MCT range		
1230.75-1231.20	CH_4, O_3, CO_2, H_2O_2, N_2O	0.37 (0.35)
1233.90-1234.20	CH_4, O_3, CO_2, H_2O_2, N_2O, solar lines	0.35 (0.33)
1234.35-1234.63	CH_4, O_3, CO_2, H_2O_2, N_2O, CH_3D	0.35 (0.33)
MW		0.68 (0.63)
$MW+MS_{[3obs]}$		0.95 (0.81)

Table 1 - Selection of microwindows (in InSb and MCT ranges) for COF_2 profile inversions. Second column lists the interfering gases adjusted during the retrievals. Last column gives the degree of freedom of the signal (DOFS) and the fraction of information coming from the measurement ($_1$) when each microwindow is fitted separately. Lines "MW" and "$MW+MS_{[3obs]}$" indicate DOFS and $_1$ when a multi-microwindows and a multi-microwindows multi-spectra fitting procedure is adopted, respectively. Solar zenithal angles of spectra used are close to 78°.

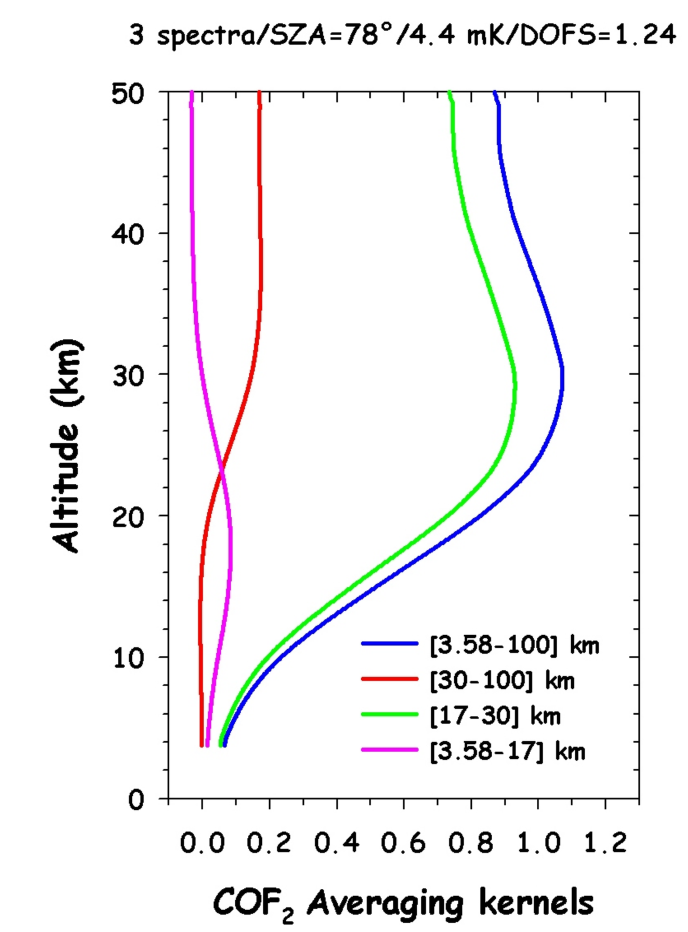

Figure 1 - Typical COF_2 averaging kernels for altitude ranges defined in the legend. These curves were obtained while applying the multi-microwindows and multi-spectra fitting procedure to the InSb microwindows defined in Table 1. Observationnal conditions and degrees of freedom of the signal (DOFS) are listed above the figure. Averaging kernels indicate that ground-based FTIR measurement is the most sensitive to COF_2 between 17 and 30 km.

3. INFORMATION CONTENT

Table 1 also demonstrates the advantage of using, simultaneously, a multi-microwindows (MW) and a multi-spectra (MS) approach for COF_2 retrievals. The last column of Table 1 provides, for each selected microwindow in each spectral range, the degree of freedom of the signal (DOFS) : this indicates how many independent pieces of information of the target gas distribution (computed for partial columns or VMR) may be derived. Values between brackets ($_1$) correspond to the first eigenvalue of the corresponding averaging kernel matrix (AvK) and indicate the fraction of the retrieved information coming from the measurement.

The line "MW" gives DOFS and $_1$ while all microwindows are fitted simultaneously. In the Insb case, one can see that a multi-microwindows fit allows to increase significantly the DOFS, but has a minor impact on information content. Only a multi-spectra fitting procedure (running with 3 spectra, for values reported in Table 1) allows to have the larger fraction of the information coming from the measurement (see line "$MW+MS_{[3obs]}$"). For the MCT range, even if a multi-microwindows fitting allows to double the DOFS and the $_1$ value, a significant improvement is reached when applying the multi-spectra approach. One COF_2 partial column can also be computed (DOFS greater or close to 1) when multi-spectra procedure is adopted. Corresponding averaging kernels indicate that most of the information is located between 17 and 30 km (Figure 1).

4. EXAMPLE OF RESULT

Right part of Figure 2 shows the evolution of polar vortex for the last days of January 2005. Jungfraujoch is identified by a black star on each map. The edge of the vortex overpass above Jungfraujoch on January 27th explains high stratospheric VMRs observed in the corresponding COF_2 profile retrieved by using the Insb set of microwindows and the multi spectra approach (left panel of Figure 2).As these polar airmasses, enriched in fluorine compounds, leave the Jungfraujoch region, COF_2 VMRs decrease to lower values. Information content related to the multi spectra approach is hence sufficient to catch such special atmospheric events. Additional tests have also demonstrated the good consistency between COF_2 partial columns and COF_2 vertical profiles retrieved from both InSb and MCT ranges.

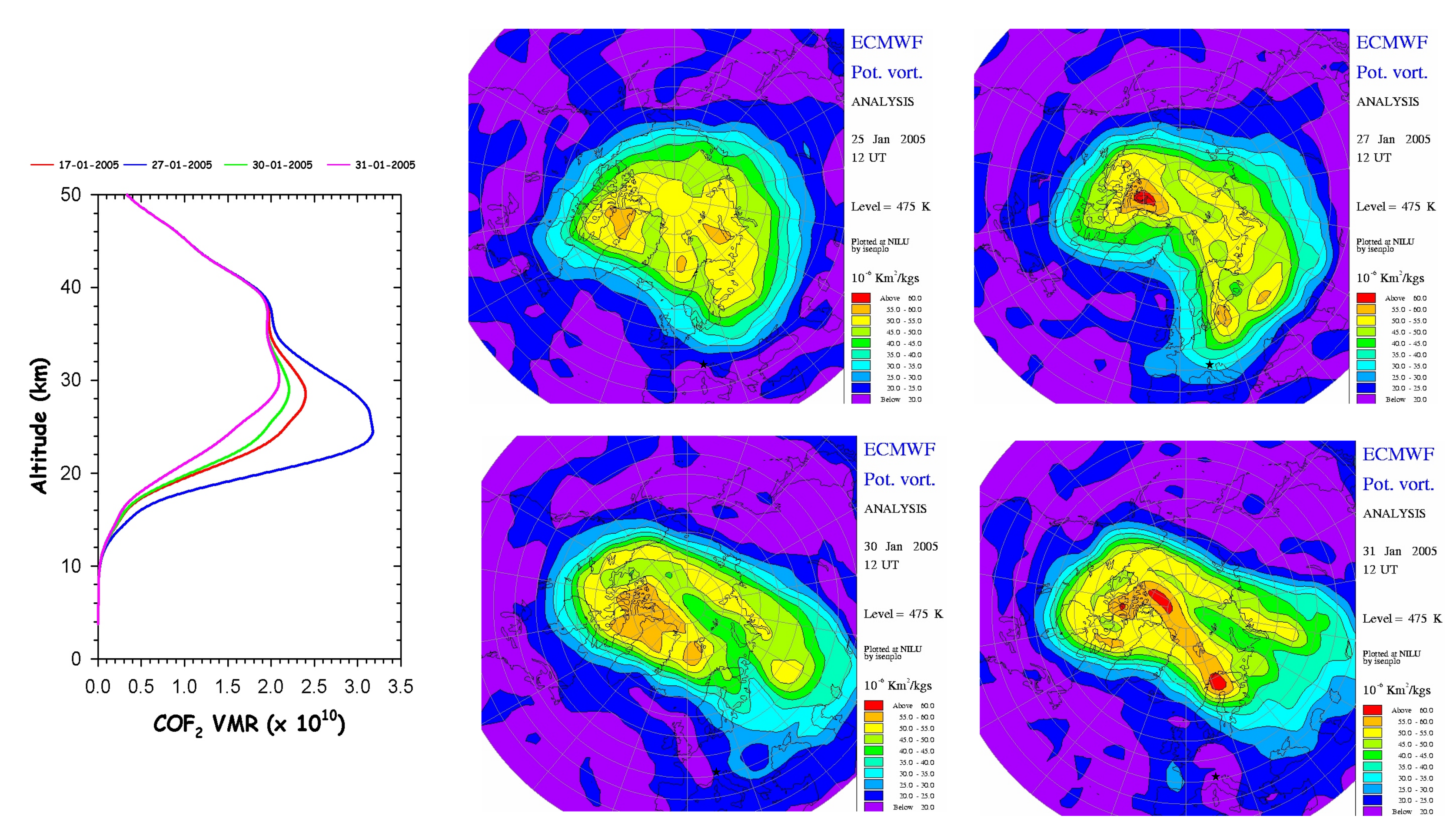

Figure 2 - Example of COF_2 vertical profiles derived from FTIR ground-based observations performed during January 2005. The overpass, above the Jungfraujoch (black star on PV maps), of the edge of the vortex, on January 27th, is well captured by the FTIR measurements (see text for details).

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