Updating hydrogen fluoride (HF) FTIR time series above Jungfraujoch: comparison of two retrieval algorithms and impact of line shape models

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NETWORK FOR THE DETECTION OF ATMOSPHERIC COMPOSITION CHANGE — NDACC — Interface between Changing Atmospheric Composition and Climate — Exploring the

1. INTRODUCTION

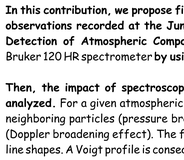
Since the first detection of hydrogen fluoride in the Earth's atmosphere [1], several studies dealing with HF total column amounts derived from ground-based Fourier transform infrared (FTIR) observations at several latitudes in both hemispheres have been published. These last years have seen the emergence of more sophisticated retrieval algorithms (e.g. SFIT-2, PROFFIT) allowing to inverse total or partial columns as well as vertical distribution of the target gas from ground-based FTIR spectra.

In this contribution, we propose first to compare HF total columns derived from FTIR high-resolution ground-based observations recorded at the Jungfraujoch (46.5°N, 8.0°E, 3580 m asl, **a primary station of the Network for the Detection of Atmospheric Composition Change - NDACC -** http://www.ndsc.ncep.noaa.gov) with a commercial Bruker 120 HR spectrometer **by using two different retrieval codes: SFIT-2 v.3.91** [2] **and PROFFIT v.9.5** [3].

Then, the impact of spectroscopic parameters (Voigt versus Galatry model line shape) on HF retrievals is also analyzed. For a given atmospheric gas, a Voigt profile takes simultaneously into account the perturbing influences of neighboring particles (pressure broadening effect) as well as the thermal translation motion of the target gas itself (Doppler broadening effect). The first effect leads to Lorentzian line shapes while the second one generates Gaussian line shapes. A Voigt profile is consequently given by the convolution of a Lorentz function with a Gaussian one.

However, as atmospheric molecules are also hindered in their free motion by collisions with the buffer gas, one can observe a narrowing of the Doppler component of the line shape ("Dicke effect" or "Dicke narrowing"). According to [4], this happens for HF when pressure is less than 290 hPa (i.e. for altitudes approximately greater than 10 km). Analytical models simultaneously including the Doppler broadening effect and the collision-induced narrowing effect exist and have been developed, for example by Galatry [5].

Full covariance matrix Sa construction



Our a priori HF profile is a zonal mean of almost 800 ACE-FTS v2.2 occultations (see Table 1). Corresponding HF measurements typically extend between 14 and 55 km. Above 55 km, the same a priori HF information used by ACE-FTS during its retrieval procedure has been adopted. For the lowest altitude levels, we have kept, for each individual profile, the HF VMR value recorded by the ACE-FTS instrument at 14km. Based on this climatological dataset, a full a priori covariance matrix Sa has been constructed, according to:

$$Sa(i,j) = E[(VMR_i - VMR_{mean,i}) \times (VMR_j - VMR_{mean,j})]$$

where E denotes the mathematical expectation. Since the covariance matrix we have obtained with ACE-FTS climatological profiles was singular (non invertible), 20% uncorrelated noise has been added on its diagonal elements.

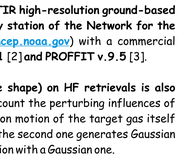


Figure 1 - HF a priori information adopted for our FTIR retrievals, deduced from ACE-FTS satellite measurements in the [41-51]°N latitude band
Left frame: a priori VMR profile; background solid lines reproduce the layering scheme adopted during our retrievals
Right frame: a priori variability profile (=diagonal elements of the full covariance matrix Sa)

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2. RETRIEVAL CODES INTERCOMPARISON

The following **regularization parameters and ancillary inputs** have been adopted (**Table 1**):

Obs. Site	Jungfraujoch (Swiss Alps, 46.5°N, 8.0°E, 3580 masl) by FTIR technique
Retrieval codes	SFIT-2 v3.91 or PROFFIT v9.5
µwindows limits + interfering gases	[4038.81– 4039.07] cm^{-1} with HF VMR profile fitted (Optimal Estimation Method, [6]) with H_2O, HDO and CH_4 VMR profiles scaled
a priori HF VMR (see Fig.1)	Mean of all ACE-FTS occultations recorded in the [41-51]°N lat. belt between Feb. 2004 and July 2008
a priori covariance (see Fig.1)	Derived from all ACE-FTS occultations recorded in the [41-51]°N lat. belt between Feb. 2004 and July 2008
spectroscopy	The official HITRAN 2004 [7]
pT profiles	Daily profiles computed for Jungfraujoch, provided by NCEP
Spectral resolution	4.10^{-3} cm^{-1}
Layering	41 layers, as illustrated on background of Fig. 1 (left frame)
Intercomparison has been performed over one year of observations at Jungfraujoch	

The year 2005 has been retained according to:
(1) the large number of observations (~200) available that year;
(2) the fact that special atmospheric events, like e.g. vortex overpass, have occurred in 2005 above Jungfraujoch - **Main results are presented in Figure 2.**

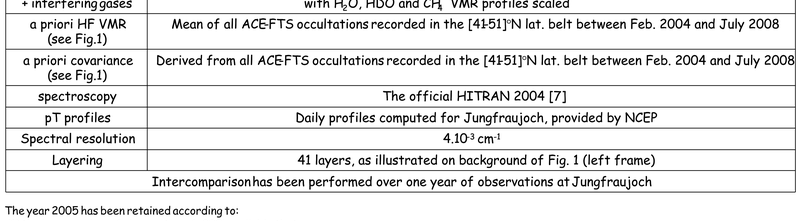
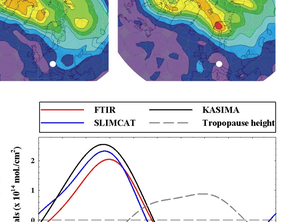


Figure 2 - **HF total column time series for the year 2005** derived from FTIR measurements at Jungfraujoch by using **regularization constraints summarized in Table 1** with two different retrieval algorithms: **SFIT 2 v3.91 (yellow dots)** and **PROFFIT 9.5 (blue dots)**. Experimental data points are individual measurements. The bottom pannel reproduces the relative difference between the two times series, computed as [(SFIT-PROFFIT)/PROFFIT]*100. **The mean relative difference (± 1-σ standard deviation) equals -0.99 ± 1.02 %, which is in excellent agreement with [3] that reports relative differences within 1%** between SFIT 2 and PROFFIT retrieved total columns of ozone, HNO_3, HDO and N_2O, respectively. The very good agreement between both retrieval codes is remarkable, **despite the fact that SFIT-2 and PROFFIT differ, notably in terms of ray tracing and radiative transfert algorithms.**
In particular, both codes are able to catch:
(1) high HF column values (e.g. on 27th January - see red circle) that can be associated to **overpasses above Jungfraujoch of polar air masses** (see corresponding potential vorticity maps on right part, where Jungfraujoch is labelled with a white dot)
(2) **the HF seasonnal cycle**, with a maximum in spring and a minimum in fall. For comparison, right bottom picture reproduces HF seasonnal cycle deduced with a statistical tool [8] from HF total column long-term time series (1996-2008) derived from FTIR measurements above Jungraujoch and from runs of 2 different numerical models (SLIMCAT [9] and KASIMA [10]). The fit fonction used is the combination of a linear term and a 3rd order Fourier series. Note also the anti-correlation that exists between the HF seasonnal cycle and the annual variation that characterizes the tropopause height above Jungfraujoch.



3. INFLUENCE OF LINE SHAPE MODEL

In [11], it has been demonstrated that, for HF inversions from its R(1) line performed with FTIR spectra recorded at Jungfraujoch, **the introduction of the collisions-induced narrowing effect allows to significantly smooth retrieved vertical profiles, mainly between 30 and 35 km**. As a direct result, the **agreement** of such FTIR HF profiles **with HALOE** HF **profiles becomes very good**, with a mean relative difference which does not excess 10% between 15 and 50 km. **In addition, this spectroscopic effect has almost no consequence on HF retrieved total columns, with differences** (relative to HF total columns obtained with a Voigt model) **lower than 1%**.

In addition to the **Voigt model**, the version 9.5 of PROFFIT is also capable to manage retrievals including a **Galatry "soft-collision" model**. **Comparisons** including both line shape models have been performed with the same set of FTIR spectra used for the intercomparison of SFIT-2 with PROFFIT. **Main results are presented in Figure 3.**

We have further quantified the **impact** of the line shape model **on error budget characterizing HF total colmun as well as 3 independant HF partial columns**. Partial columns limits were deduced from HF information content analysis and cover the lowermost part of the stratosphere (10-17 km, LOS), the lower-middle stratosphere (17-25 km, LMS) and the middle-upper stratosphere (25-40 km, MUS), respectively. **Main results are presented in Table 2.**

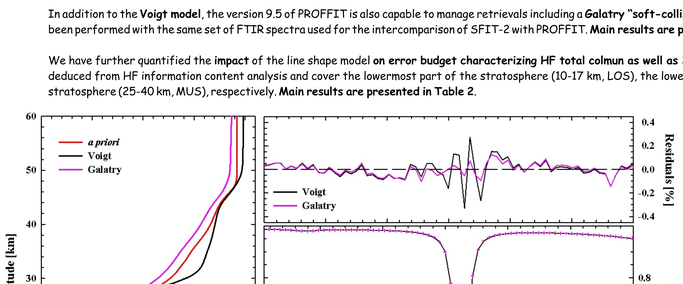


Figure 3 - Impact of line shape model (Voigt vs Galatry) on HF retrieved vertical profiles and on fitting quality.

Left panel: **mean HF profiles (for the year 2005) retrieved with PROFFIT 9.5 and assuming Voigt line shape (black line) or Galatry line shape (pink line)**. The **a priori profile** adopted for the retrievals is plotted **in red**. Like in [11], we observe a **significant smoothing** of HF profiles **when the Galatry model is used**, mainly **between 25 and 40 km**. A small but significant **relative difference** (computed over the whole year 2005) **between corresponding HF total columns** of **1.18 ± 0.29 %** was found (the error corresponds to 1-σ standard deviation), in good agreement with [11].

Right panel – bottom frame: typical example of **synthetic spectra obtained for HF with a Voigt model (black line) and with a Galatry model (pink crosses)**. These two spectra were calculated during the adjustment of a FTIR observation (not shown here) recorded at ISSJ on January 8, 2005 **at a solar zenith angle close to 73°**. For each case, **corresponding residuals** (measured minus simulated spectrum) **are plotted on top frame**. A **major improvement** is reached **when the Galatry model is adopted**. In particular, systematic symmetric features observed in the center of the HF signature when the Voigt model is used are significantly reduced when the Galatry approach is applied. The **mean relative difference** (for all FTIR observations of 2005) calculated as [(Voigt-Galatry)/Galatry] x 100 **between residuals obtained with both models is 18.97 ± 13.17 %** (± 1-σ standard deviation). This result highlights the fact that a Galatry line shape model definitely improves HF retrievals quality.

	Total column [3.58-86.8] km	LOS [10-17] km	LMS [17-25] km	MUS [25-40] km
Systematic errors				
Spectroscopy	4.95±0.02 *4.96±0.01*	6.49±0.39 *5.97±0.25*	5.50±0.20 *5.32±0.24*	6.56±0.11 *6.46±0.05*
Temperature profile	0.20±0.01 *0.20±0.01*	1.57±0.27 *1.06±0.10*	0.67±0.22 *0.82±0.21*	0.68±0.08 *0.55±0.04*
Solar parameters	0.02±0.01 *0.02±0.01*	0.24±0.16 *0.17±0.12*	0.03±0.02 *0.04±0.03*	0.02±0.01 *0.01±0.01*
Line of sight	0.20±0.15 *0.20±0.15*	0.22±0.18 *0.22±0.18*	0.23±0.17 *0.22±0.17*	0.26±0.20 *0.26±0.22*
ILS	0.59±0.16 *0.58±0.11*	5.08±1.31 *2.96±0.86*	3.00±0.58 *3.22±0.48*	2.89±0.35 *2.25±0.33*
Baseline	0.06±0.01 *0.06±0.01*	0.11±0.05 *0.09±0.02*	0.03±0.01 *0.03±0.01*	0.12±0.05 *0.11±0.04*
TOTAL	**6.03±0.32** ***6.03±0.26***	**13.71±1.54** ***10.47±1.09***	**9.47±0.58** ***9.65±0.35***	**10.54±0.59** ***9.64±0.49***

Table 2 - **Main systematic (left) and statistical (right) errors (in percents) for HF total and partial columns at Jungfraujoch (straight values stand for a Galatry line shape model, italic values are for a Voigt model)**. Errors given here are mean values computed over a sample of 5 FTIR spectra. Associated **uncertainties are two times the standard error on the mean**. **Apart from** errors due to **spectroscopy, spectral noise, temperature profile and ILS**, it is clear from that for all other error sources and for all altitude ranges reported, **the choice of line shape model has very limited impact**. For the errors due to spectroscopy, spectral noise and ILS, the main difference between both line shape models is observed in the lowermost stratosphere (LOS), where the Voigt model gives lower error values. These differences are however non significant, regarding uncertainties characterizing these errors. Considering error due to spectroscopy, it remains the main source of systematic error. **The only significant improvement observed between both models (underline values)** is observed for the systematic and statistical contributions associated to **temperature profile error in the LOS and MUS regions**, where the Voigt model reduces corresponding errors. These differences are **probably ascribable to different dependences in temperature of both Voigt and Galatry models. As a consequence** of the general improvement by **the Voigt model in the LOS region, the total systematic error is significantly reduced by a few percents** when adopting this line shape model. However, this improvement remains weak compared to the significant improvement value observed in the fitting quality (see Figure 3).

Errors description

The error tool of PROFFIT 9.5 allows to estimate the individual contribution associated to seven different error sources: the spectroscopy (including both half-width and line intensity errors), the temperature profile, solar parameters (including line intensity and spectral horizontal scale), the line of sight, the instrumental line shape (ILS, including both modulation and phase contributions), the baseline (including both offset and channeling contributions) and the spectral noise. This latter error source is directly estimated from FTIR spectra during the retrieval process.

For the following error sources, we have assumed these systematic weights: temperature profile = 30%, solar parameters = 20%, line of sight = 10%, ILS = 50% and baseline = 50%.

	Total column [3.58-86.8] km	LOS [10-17] km	LMS [17-25] km	MUS [25-40] km
Statistical errors				
Noise	0.47±0.13 *0.59±0.14*	8.76±3.63 *6.73±2.41*	2.97±0.67 *3.90±0.51*	1.62±0.45 *1.31±0.41*
Temperature profile	0.46±0.03 *0.47±0.02*	3.66±0.63 *2.47±0.22*	1.57±0.52 *1.91±0.49*	1.59±0.18 *1.29±0.08*
Solar parameters	0.07±0.03 *0.07±0.03*	0.98±0.64 *0.70±0.50*	0.13±0.07 *0.16±0.11*	0.06±0.05 *0.04±0.04*
Line of sight	1.84±1.39 *1.72±1.50*	1.94±1.59 *1.88±1.67*	2.00±1.49 *1.85±1.64*	2.34±1.80 *2.19±1.89*
ILS	0.59±0.16 *0.58±0.11*	5.08±1.31 *2.96±0.86*	3.00±0.58 *3.22±0.48*	2.89±0.35 *2.25±0.33*
Baseline	0.06±0.01 *0.06±0.01*	0.11±0.05 *0.09±0.02*	0.03±0.01 *0.03±0.01*	0.12±0.05 *0.11±0.04*
TOTAL	**2.14±1.26** ***2.13±1.27***	**11.43±3.21** ***8.37±1.93***	**5.21±0.71** ***5.98±0.59***	**4.58±1.28** ***3.92±1.32***

Acknowledgements - This research has essentially been supported by the Belgian Federal Science Policy Office, Brussels (SECPEA project). Additional support by the EC-GEOmon project is further acknowledged. We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG, Bern) and the University of Liège for supporting the facilities needed to respectively perform the observations and their analyses. Thanks are extended to all collaborators having contributed to the observations at the Jungfraujoch. Thanks are also going to all the members of the ACE-FTS experiment for providing data. We also thank the ECMWF for making their PV maps used in this work available. We are grateful to F. Hase and M. Schneider of IMK-IFU, Karlsruhe for strong support during the learning phase of the PROFFIT code.