First retrievals of HCFC-142b from ground-based high resolution FTIR solar observations: application to high altitude Jungfraujoch spectra

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INSTRUMENTATION, SITE, OBSERVATIONAL DATABASE AND TOOLS

-- Two Fourier Transform InfraRed (FTIR) spectrometers, namely a homemade and a Bruker IFS120-HR, are operated under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (Swiss Alps, 46.5ºN, 8.0ºE, 3580m a.s.l.). This site is located on the saddle between the Jungfrau (4158m) and the Mönch (4107m) summits. FTIR monitoring activities are conducted at that site within the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, see http://www.ndacc.org). More information on the involvement of the University of Liège at the Jungfraujoch station since the early 1950s as well as on some representative achievements can be found in Zander et al. [2008].

-- Both instruments are equipped with cooled HgCdTe and InSb detectors, allowing covering the 650 to 4500 cm^{-1} region of the electromagnetic spectrum. Here, we use high-resolution (0.006 cm^{-1}, OPD of 82 cm) IR solar absorption spectra spanning the 700-1400 cm^{-1} interval. Given the weak absorption of HCFC-142b, we selected spectra recorded at low sun, with apparent zenith angle in the 80-87º range (about 3000 spectra available, of which ~2200 recorded with the Bruker instrument). Average signal-to-noise ratio is close to 900.

-- All retrievals have been performed with the SFIT-2 algorithm (v3.91) which is based on the semi-empirical implementation of the Optimal Estimation Method of Rodgers [1990]. This code allows in most cases to retrieve information on the vertical volume mixing ratio (vmr) profile of the species accessible to the ground-based FTIR technique. Here however, only scaling of the a priori vertical distribution of HCFC-142b has been allowed.

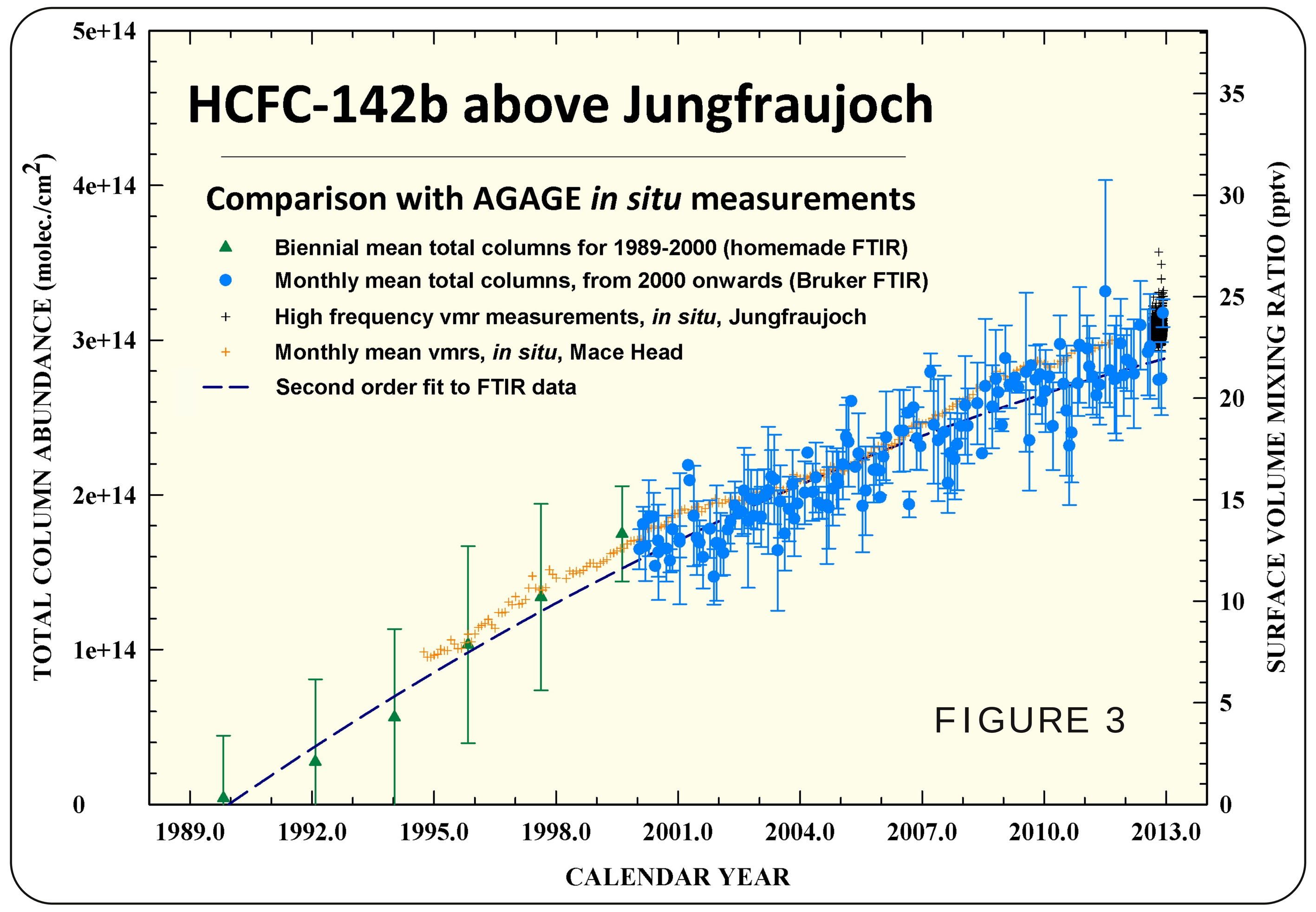
BACKGROUND INFORMATION ON HCFC-142b (CH_3CClF_2)

-- Hydrochlorofluorocarbons (HCFCs) are the first substitutes to the long-lived ozone depleting halocarbons, in particular the man-made chlorofluorocarbons (CFCs).

-- Given the complete ban of the CFCs by the Montreal Protocol and its Amendments and Adjustments, HCFC emissions have been rising, with a wide use of these compounds in many applications, e.g. as foam blowing agents, in refrigeration and air-conditioning.

-- Current emissions of HCFC-142b are significant, on the order of 35 Gg/yr. Its atmospheric accumulation has recently accelerated, and present growth rates amount to 1.1-1.2 pptv/yr. The HCFC-142b vmr is now close to 25 pptv in the northern hemisphere (Montzka et al., 2011).

-- The HCFC-142b atmospheric lifetime is estimated at 18 years. With a global warming potential of 2310 on a 100-yr time horizon, it is also a potent greenhouse gas (Foster et al., 2007).



SELECTION AMONG THE CANDIDATE WINDOWS FOR THE RETRIEVAL OF HCFC-142b

Using HITRAN 2008 [Rothman et al., 2009], averaged vmr profiles based on WACCM version 6 model predictions for the 1970-2020 time period [the Whole Atmosphere Community Model, http://waccm.acd.ucar.edu], mean humidity conditions for the Jungfraujoch and a HCFC-142b vertical distribution scaled to match its mean 2012 abundance, we have computed synthetic spectra (6.1 mk, zenith angle of 82.5º) for the first and second order absorbers in four candidate windows for the retrieval of HCFC-142b. The windows in the 900 and 1100 cm^{-1} regions are shown in **FIGURE 1** and **FIGURE 2**, respectively. The individual absorptions are reproduced using different color codes and most have been shifted vertically for clarity. Identification of the absorbing gas is provided on the right hand side of the simulations.

As noticeable when comparing the HCFC-142b features from each frame (continuous pink lines), the absorptions are stronger in Figure 2 than in Figure 1. Numerical values indicate maximum absorptions of 1.1% near 1193 cm^{-1}, 0.7% near 1135 cm^{-1}, 0.5% near 905 cm^{-1} and 0.3% near 967.5 cm^{-1}. However, and as confirmed by fits to these windows, strong interfering absorptions by CO_2, O_3 and H_2O prevent reliable retrievals of HCFC-142b from the ground in the 965-970 and 1132-1136 cm^{-1} intervals, even at the dry high altitude site of the Jungfraujoch. The situation is more favorable in the 900-906 and 1191-1196 cm^{-1} windows. But systematic and independent fits to both domains have revealed that adoption of the second interval led to the determination of total columns too large by about a factor of 2, possibly resulting from a missing interference in HITRAN and/or inconsistent cross section parameters for HCFC-142b. It should be mentioned that the Newnham and Ballard [1995] cross sections, converted to pseudolines by G.C. Toon, JPL, were used here; the new cross-sections of Le Bris and Strong [2010] have not been tested yet. In contrast, the 900-906 cm^{-1} interval provided total columns and corresponding vmrs for HCFC-142b in the expected range. This feature was therefore selected for sytematic retrieval of HCFC-142b from the Jungfraujoch.

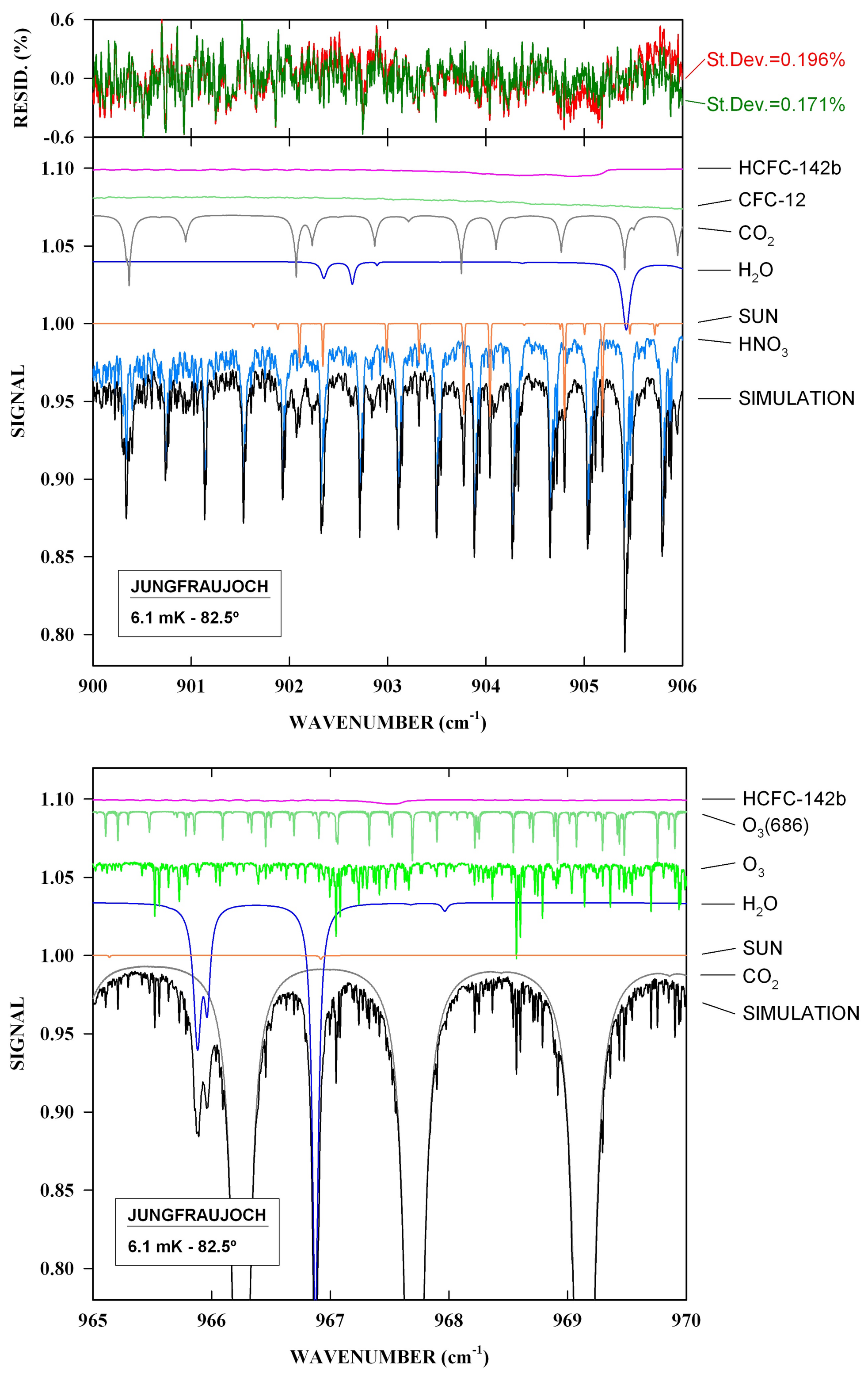


FIGURE 1

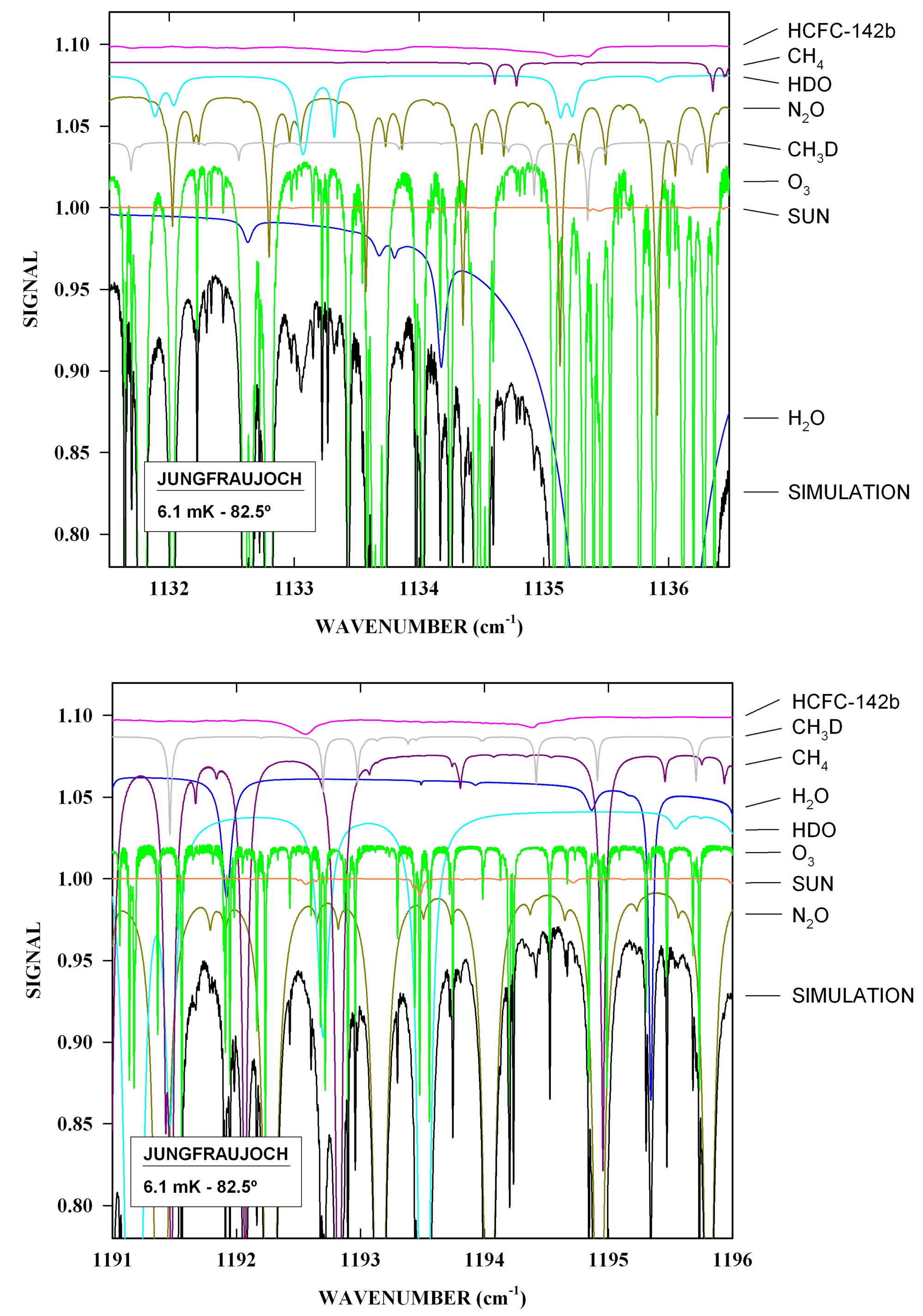


FIGURE 2

RETRIEVAL STRATEGY AND FIRST FTIR TIME SERIES FOR HCFC-142b

-- Available spectra were fitted, adopting the following settings: (i) a first run was performed to pre-fit CFC-12, (ii) the vmr profiles of HNO_3 and H_2O were retrieved during the iterative process while the a priori distributions of CO_2, HCFC-142b were scaled, using a window spanning the 900-906 cm^{-1} interval (iii) line parameters from the HITRAN 2008 compilation were used and (iv) we assumed mid-day pressure and temperature profiles provided by the National Centers for Environmental Predictions (NCEP, see http://www.ncep.noaa.gov). Typical residuals from the fit to a spectrum recorded on November, 20, 2012 are shown on the upper frame of Figure 1, in green when including HCFC-142b in the retrieved species, in red when assuming no HCFC-142b in the atmosphere. Uncertainties on the total columns have been evaluated, accounting for various error sources (temperature profile, instrumental line-shape, finite S/N, a priori profile for the target gas, uncertainties on the line parameters...) to <8% and <12%, for the total random and systematic contributions.

-- **FIGURE 3** reproduces the total column time series of HCFC-142b above Jungfraujoch, normalised to 654 hPa. Blue circles correspond to monthly mean total columns derived from Bruker observations while the green triangles show biennial total column averages derived from early spectra recorded with the homemade spectrometer. In both cases, error bars display the standard deviation around the mean. Among striking features, we see a significant build up of HCFC-142b in the atmosphere, with a yearly column increase of (1.05±0.08) E13 molec./cm^2 (2-σ) for 2000-2012, or (6.5±0.5) %/yr when taking the 2000.0 column as reference.

-- AGAGE GC-MS *in situ* measurements at Mace Head (53ºN) and Jungfraujoch have been reproduced in Figure 3 for comparison, as orange and black crosses, respectively (refer to right axis scale). Overall, the long-term evolution of the *in situ* and FTIR time series are commensurate, with the latter data lower by 5% on average, i.e. within the systematic uncertainty evaluated above.

REFERENCES

• Foster, P. et al., Changes in Atmospheric Constitutents and in Radiative Forcing, contribution of WG I to the fourth Assessment Report of IPCC, 2007.
• Le Bris, K., and K. Strong, Temperature-dependent absorption cross-sections of HCFC-142b, JQSRT, 111, 2010.
• Montzka, S.A., S. Reimann, A. Engel et al., Ozone-Depleting Substances (ODSs) and Related Chemicals. Chapter 1 in Scientific Assessment od Ozone Depletion: 2010, Report No. 52, World Meteorological Organization, 2011.
• Newnham, D., and J. Ballard, Fourier transform infrared spectroscopy of HCFC-142b vapour, JQSRT, 53, 1995.
• Rodgers, C.D., Characterisation and error analysis of profiles derived from remote sensing measurements, J. Geophys. Res., 95, 5587-5595, 1990.
• Rothman, L.S., I.E. Gordon, A. Barbe et al., The HITRAN 2008 molecular spectroscopic database, JQSRT, 110, 2009.
• Zander, R., E. Mahieu, P. Demoulin et al., Our changing atmosphere: Evidence based on long-term infrared solar observations at the Jungfraujoch since 1950, Sci. Total Environ., 391, 184-195, 2008.

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