# First HFC-134a retrievals and analysis of long-term trends from FTIR solar spectra above NDACC network stations: the Jungfraujoch case

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#### Introduction

Since the discovery of the chlorofluorocarbons (CFCs) implication in stratospheric ozone destruction, the Montreal Protocol (1987) has aimed at controlling the production of CFCs and other ozone depleting substances (ODS) in order to protect and then recover the ozone layer. Consequently, temporary substitutes for CFCs have been developed and produced by the industry. First substitute molecules were hydrochlorofluorocarbons (HCFCs), which have smaller ozone depletion potentials (ODP) than CFCs since their atmospheric lifetimes are shorter. Nevertheless, HCFCs still contain chlorine atoms and hence, also deplete the stratospheric ozone, requiring them to be banned in turn. Thus, chlorine-free molecules, i.e. hydrofluorocarbons (HFCs) such as CH<sub>2</sub>FCF<sub>3</sub> (HFC-134a) were introduced to replace both CFCs and HCFCs. HFC-134a is mainly used for mobile and domestic refrigerators, air-conditioning, aerosol propellant and as a blowing agent. Even if HFCs do not contribute to ozone depletion, they are very powerful greenhouse gases. They have great global warming potentials (100-year GWP for HFC-134a is 1470 (WMO, 2022)). Consequently, the Kigali amendment (2016) to the Montreal Protocol aimed for their phase-out.

The atmospheric concentrations of CFCs have decreased in response to the phase-out and ban of their production by the Montreal Protocol and its subsequent amendments, while the HCFCs burden is now leveling off. In contrast, the atmospheric concentrations of HFCs have increased notably in the last two decades. Consequently, monitoring HFC-134a atmospheric concentrations is necessary as a support of the Montreal Protocol and concretely the Kigali amendment.

Poster presented at the **EGU General Assembly 2023** 23-28 April 2023 Vienna (Austria)







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#### **NDACC FTIR observations**

The High Altitude Research Station Jungfraujoch is located on the Northern Swiss Alps (46.55°N, 7.98°E) at 3580 m above mean sea level (a.m.s.l.). Retrievals of HFC-134a total columns above Jungfraujoch are carried out using SFIT-4 (v1.0.18) algorithm implementing the Optimal Estimation Method (OEM) of Rodgers (2000). The retrievals are performed using harmonized layering schemes. 41 layers are defined, with thicknesses increasing progressively from the site altitude (3.58 km) up to 120 km. The period of study currently covers 27 years (1996 - 2022).

### First HFC-134a retrievals above Jungfraujoch

Several spectral windows have been tested for this work. Two of them have been chosen (1104.2–1105.5 cm<sup>-1</sup> and 1182.0–1187.0 cm<sup>-1</sup>). The first window has been selected as the best one since water vapour interference is minimum.





**Figure 1:** Simulations of the 1104.2–1105.5 cm<sup>-1</sup> spectral window from spectra recorded by the Bruker IFS-120HR FTIR instrument at Jungfraujoch station with an apparent solar zenith angle of 77.2°. The root-mean-square of the fitting residuals (RMS) is 0.29%. The main interfering species ( $H_2O$ ,  $O_3$ ,  $CO_2$ , O3668, and O3686) are shifted vertically for clarity. Second-order absorbers are not shown. The top panel displays the observed-calculated residuals, in %, from the fit to the spectrum recorded on 25 May 2016. The bottom panel shows the absorption of the target species (around 0.4%).



#### Long-term trend analysis



**Figure 2:** FTIR monthly time series of HFC-134a dry air mole fractions (xHFC-134a) above Jungfraujoch. All vertical bars represent the standard deviations around the monthly means. Total columns have been derived from solar spectra recorded by the Bruker IFS-120HR spectrometer and then transformed into xHFC-134a. Data from the period June 2011 – December 2012 is still under analysis due to a reduction of the instrument performance. For more information see Prignon et al. (2019). The period previous to 2000 has not been included for the trend calculations since the increase is not very significant.

#### **Prospects**

- Extend the FTIR Jungfraujoch time series back to mid-1980s.
- consistent with other networks time series.
- The bias between ACE-FTS and FTIR trends has still to be studied.

#### **References and acknowledgments**

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The University of Liège team has been primarily supported by the Fonds de la Recherche Scientifique (F.R.S.-F.N.R.S., Brussels, Belgium; grants J.0147.18 and J.0126.21) and by the GAW-CH program of MeteoSwiss (Zürich, Switzerland). E. Mahieu is a senior research associate with the F.R.S.-F.N.R.S. We thank Dr G. C. Toon (Caltech-JPL) for developing, maintaining and making available the pseudolinelists (PLLs) that were essential to the present work. We thank the whole GIRPAS team for their contribution and support.



**Figure 3:** HFC-134a annual mole fractions and projections from different networks. Image adapted from WMO (2022) Figure 2-1.

The HFC-134a global trend from January 2004 to December 2018 using ACE-FTS satellite data between 5.5 and 24.5 km is 4.49  $\pm$  0.02 ppt yr<sup>-1</sup> and global SLIMCAT model trend is 4.66 ppt  $yr^{-1}$  as reported by Harrison et al. (2021).

• Retrieving HFC-134a from FTIR observations has been demonstrated. They are

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