High resolution solar infrared Fourier transform spectrometry: application to the study and long-term monitoring of the Earth's atmosphere

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1. Project description

The Liège team has a long tradition in the monitoring of the Earth's atmosphere. Indeed, the first observations and investigations were carried out by Prof. Marcel Migeotte and collaborators in the late 1940s, using a grating infrared spectrometer. This instrument was then installed at the Jungfraujoch station and infrared spectra were systematically recorded in 1950-1951 such as to cover the 2.8 to 23.7 micrometer (µm) spectral range (Migeotte et al., 1956). The next two decades were dedicated to the study of the sun and to the production of photometric solar atlases, using a 7 m grating spectrometer, in single then double pass mode. In the mid-1970s, the team resumed its atmospheric monitoring activities, which are still ongoing nowadays. Since the mid-1980s, Fourier Transform InfraRed (FTIR) instruments have been used, allowing to record very high resolution and signal-to-noise wide-band solar infrared spectra. This sustained effort has led to an unrivalled collection of infrared spectra, which is unique worldwide in terms of length, measurement density and quality. This exceptional achievement resulting from a fruitful and long-lasting collaboration between Switzerland and Belgium has been acknowledged by the European Chemical Society: the EuChemS Historical Landmark Award has been granted to the Jungfraujoch High Altitude Research Station, in recognition of the pioneering work and exceptional "liaison réussie" between the research group of Prof. Marcel Migeotte (1912-1992) with collaborators from the University of Liège, Belgium, and the International Foundation of the High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG), Switzerland. This was celebrated during a one-day symposium in Bern on Thursday, February 16, followed by the official award ceremony at the Jungfraujoch on Friday, February 17, 2023 (see https://ehla23.scg.ch/).

The current main objectives of the team are essentially twofold: (i) maintain the instrumentation operational while also improving its performance, (ii) analyse the spectra to produce high-level geophysical parameters and valorise them.

In 2023, solar observations have been collected remotely, but also onsite in October. Altogether and before any averaging, about 1600 high resolution infrared solar spectra were collected on 50 days. There are spectra available on at least one day for all months but March.

Table 1. List of atmospheric species currently retrieved from the Jungfraujoch observational database. The two new species added in 2023 are underlined.

Greenhouse gases; support to the Paris Agreement	H_2O, CO_2, CH_4, N_2O, CF_4, SF_6
Ozone-related; support to the Montreal Protocol	O_3, NO, NO_2, HNO_3, $ClONO_2$, HCl, HF, COF_2, CFC-11, CFC-12, HCFC-22, HCFC-142b, CCl_4, CH_3Cl, <u>HFC-134a</u>, <u>HFC-23</u>
Air quality; support to the EU-Copernicus programme	CO, CH_3OH, C_2H_6, C_2H_2, C_2H_4, HCN, HCHO, HCOOH, NH_3, PAN
Other	OCS, N_2, various isotopologues[1]

[1]) an isotopologue is a molecular twin that differs from the reference molecule in the isotopic composition.

The systematic analysis of our spectra allows us to determine the abundance of an increasing number of key constituents of the Earth atmosphere (currently more than 35, see Table 1), playing a role in ozone depletion, climate change, or affecting air quality. Numerous target species are therefore relevant to the Montreal Protocol on substances that deplete stratospheric ozone (e.g., CFCs, HCFCs, HFCs, HCl) and/or to the Paris Agreement (COP21) to mitigate climate change (e.g., CO_2, CH_4, N_2O). It is also worth noting that long-lived tracers such as, e.g., HCl, HF, N_2O, can also be used to provide useful insights regarding global atmospheric circulation.

2. Research highlights

The Kigali Amendment (2016) to the Montreal Protocol entered into force in 2019. This amendment targets a gradual reduction of the production and use of long-lived HFCs, the second family of substitutes to the CFCs widely used in the air conditioning and refrigeration sectors, given their adverse effects on climate.

In 2023, we investigated whether such compounds could be retrieved from our FTIR spectra, and we started with two candidates, namely HFC-134a (CH_2FCF_3) and HFC-23 (CHF_3), the two most abundant HFCs in the Earth's atmosphere. Both species have exploitable spectral features, near 1105 and 1155 cm^{-1}, for HFC-134a and HFC-23, respectively. These absorptions are weak, typically of less than 1%, and the retrieval of these compounds is very challenging. Retrieval approaches have been developed and carefully tuned such as to minimize the effect of the interferences (mainly by ozone, nitrous oxide, or water vapour lines) as well as the random uncertainty affecting the retrieved total columns.

For HFC-23, the relative uncertainty typically amounts to ≈11 % for a single measurement, with the leading contribution to the error budget coming from the uncertainties on the temperature vertical profiles. For HFC-134a, the typical random error amounts to ≈10 %, the error budget being dominated by the measurement and interference errors. In both cases, only total columns can be retrieved as there is no vertical sensitivity available.

FTIR time series have been retrieved for both species, they have been compared with *in situ* and satellite datasets, and trends have been determined using a statistical tool based on the autoregressive wild bootstrap method (Friedrich et al., 2020, and references therein). For HFC-23 a time series has been derived for the 2007-2020 period. When considering the monthly means and a linear increase, a relative trend of (3.71±0.23) %/yr is obtained, demonstrating a significant buildup of HFC-23 in the Earth's atmosphere. Commensurate values are determined when considering other available datasets, i.e. (4.12±0.27) %/yr for Atmospheric Chemistry Experiment-FTS (ACE-FTS) satellite occultation measurements (version 5.0; Boone et al., 2023) available for the same time interval above the "Switzerland area" (40-60°N; -5°W-15°E), and (3.61±0.07) %/yr for *in situ* surface measurements performed by the AGAGE network at Mace Head (53°N, Ireland). More information can be found in Hiault (2023). As for HFC-134a, Figure 1 shows as orange dots the FTIR yearly mean time series over 2004-2022 for the HFC-134a dry air mole fractions, or xHFC-134a, in ppt. Here also, our time series is compared with independent datasets available from ACE-FTS (version 5.2, in the 40-50° latitudinal band), AGAGE (Jungfraujoch station, Empa) and a TOMCAT model simulation (refer to the color key provided in the figure and its caption for the identification of the datasets). Considering the monthly mean time series and assuming a linear increase of HFC-134a, we derive relative trends (with respect to mean values over 2004-2022) of (7.34±0.16) %/yr for the FTIR data, (7.29±0.16) %/yr for the ACE-FTS data, (6.61±0.05) %/yr for the AGAGE *in situ* surface baseline time series and (7.12±0.05) %/yr for TOMCAT. The corresponding absolute annual increase rates are in the 5.0-5.5 ppt range. More information to appear soon in Pardo Cantos et al. (2024).

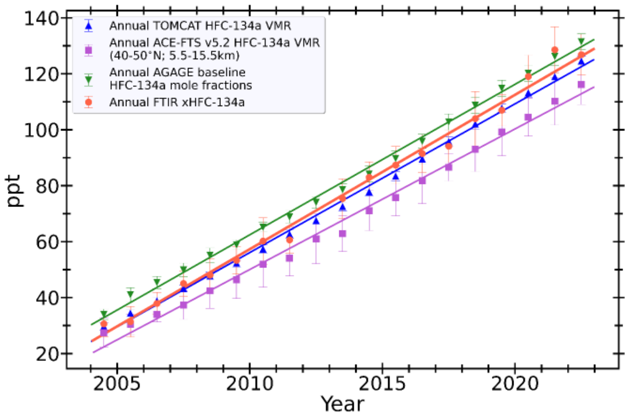

Figure 1. The atmospheric HFC-134a annual mean time series as derived from the Jungfraujoch FTIR (in terms of xHFC-134a data; see orange dots), compared with the TOMCAT HFC-134a lowermost model level VMRs (as blue up-pointing triangles); with the ACE-FTS v5.2 HFC-134a VMRs (as purple squares); and with the in situ baseline HFC-134a mole fractions at Jungfraujoch (as green down-pointing triangles). The error bars depict one standard deviation.

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Internet data bases

http://girpas.uliege.be/
www-air.larc.nasa.gov/pub/NDACC/PUBLIC/stations/jungfraujoch/hdf/ftir/
www-air.larc.nasa.gov/pub/NDACC/PUBLIC/RD/jungfraujoch/hdf/ftir/
Data are also available upon request (emmanuel.mahieu@uliege.be)

Collaborating partners / networks

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