Seeking for the optimum retrieval strategy of methanol (CH_3OH) using ground-based high-resolution FTIR solar observations recorded at the high-altitude Jungfraujoch station (46.5°N)

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INSTRUMENTATION, SITE, OBSERVATIONAL DATABASE AND TOOLS

-- Two high-resolution Fourier Transform InfraRed (FTIR) spectrometers are operated under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (ISSJ, Swiss Alps, 46.5°N, 8.0°E, 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 spectrometers are equipped with HgCdTe and InSb cooled detectors, allowing covering the 650 to 4500 cm^{-1} region of the electromagnetic spectrum. For the present investigations, we use high-resolution (0.004 and 0.006 cm^{-1}) IR solar absorption spectra spanning the 700-1400 cm^{-1} interval. They have been recorded year-round, on a regular basis, with a Bruker IFS-120HR instrument. Although such spectra are available since the early 1990s, we focus here on a subset of our database and only include observations recorded from 2005 onwards. Signal-to-noise ratios are on average close to 800.

-- 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 case to retrieve information on the vertical volume mixing ratio (vmr) profile of the species accessible to the ground-based FTIR technique.

BACKGROUND INFORMATION ON METHANOL (CH_3OH)

-- Methanol (CH_3OH) is a key organic compound in the Earth's atmosphere, with reported concentrations of the order of a few ppbv

-- It is therefore the second most abundant atmospheric organic compound after methane (CH_4), despite an estimated lifetime of a few days [Jacob et al., 2005]

-- Natural sources of CH_3OH include plant growth, oceans, decomposition of plant matter, oxidation of methane...

-- Anthropogenic sources are from vehicles, industry...; biomass burning completes the emission budget

-- The main sink is oxidation by the hydroxyl radical, leading to the formation of carbon monoxide (CO) and formaldehyde (H_2CO) [e.g. Rinsland et al., 2009; Stavrakou et al., 2011, and references therein]

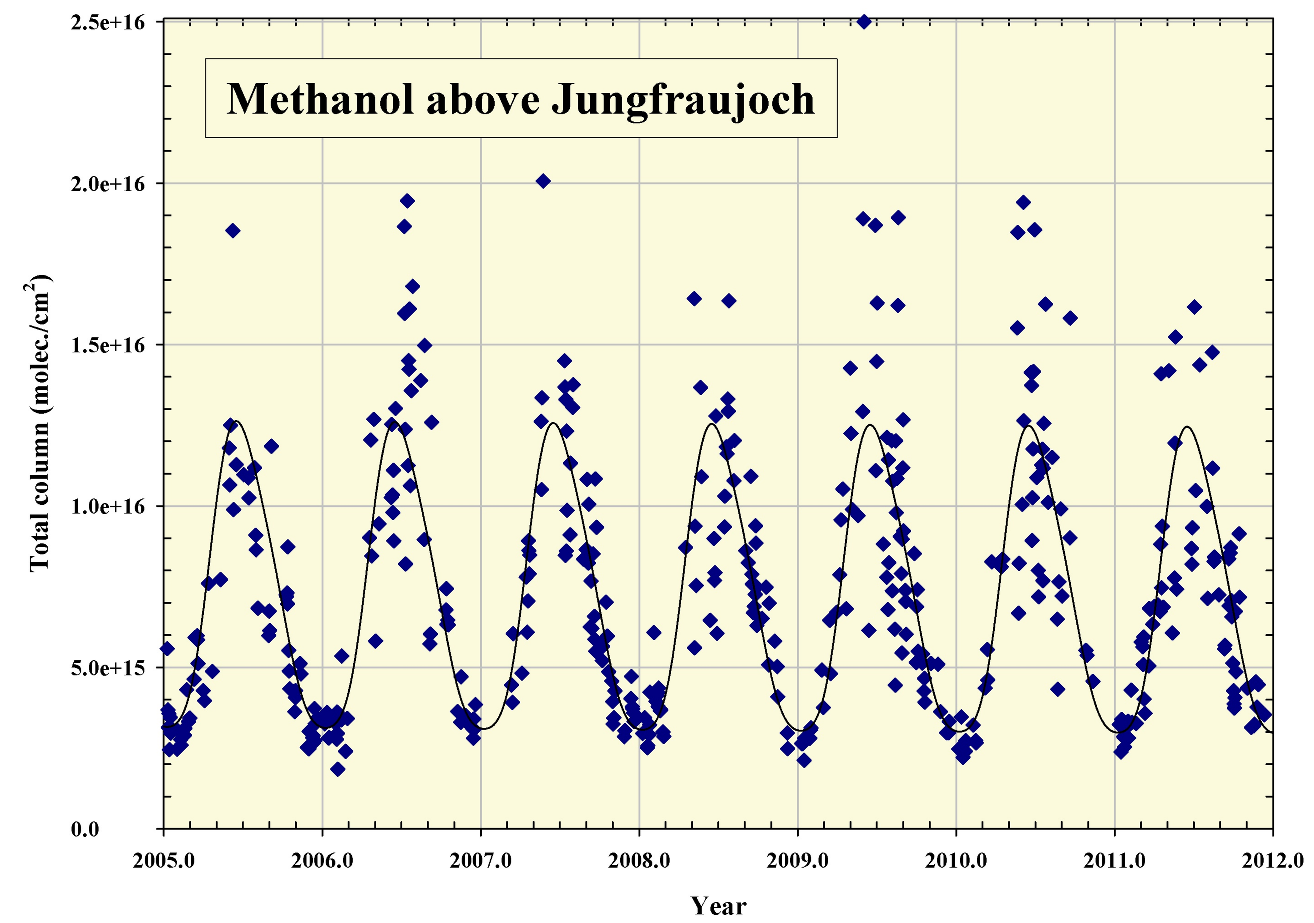

FIGURE 4

SIMULATIONS OF TWO METHANOL WINDOWS FOR THE JUNGFRAUJOCH STATION

Using HITRAN 2008 [Rothman et al., 2009] and averaged vmr profiles based on WACCM model predictions for the 1970-2020 time period [the Whole Atmosphere Community Model, http://waccm.acd.ucar.edu], we have computed synthetic spectra (6.1 mk, zenith angle of 80°) for the first and second order absorbers in two CH_3OH windows. They range from 992 to 999 cm^{-1} and from 1029 to 1037 cm^{-1} and encompass features of the strong nu8 band of CH_3OH. These intervals were used for the retrieval of CH_3OH by Rinsland et al. [2009] and Stavrakou et al. [2011], respectively. The individual absorptions are reproduced using different color codes in the two frames of **FIGURE 1**, most have been shifted vertically for clarity. Identification of the absorbing gas is provided on the right hand side of the simulations.

Absorption by the main ozone isotopologue (^{16}O-^{16}O-^{16}O, or O_3) is prominent, particularly in the second window where it captures nearly 93% of the IR radiation, i.e. much closer to saturation than in the first window (29%). Methanol features are much weaker, with mean absorptions of 1.4 and 1.6% in the "999" and "1037" windows, respectively. Additional significant absorptions are associated to several ozone isotopologues (e.g. O3686, for ^{16}O-^{18}O-^{16}O, O3668), carbon dioxide (CO_2) and water vapor (H_2O).

All relevant 2010 spectra recorded with zenith angles between 75 and 85° have been independently fitted to retrieve CH_3OH in the selected windows. We display in **FIGURE 2** a scatter plot of the two total column data sets demonstrating a very compact correlation. There is no significant bias between the two regions, with a mean relative difference between the corresponding total columns of -(0.6±3.0)% (1-sigma).

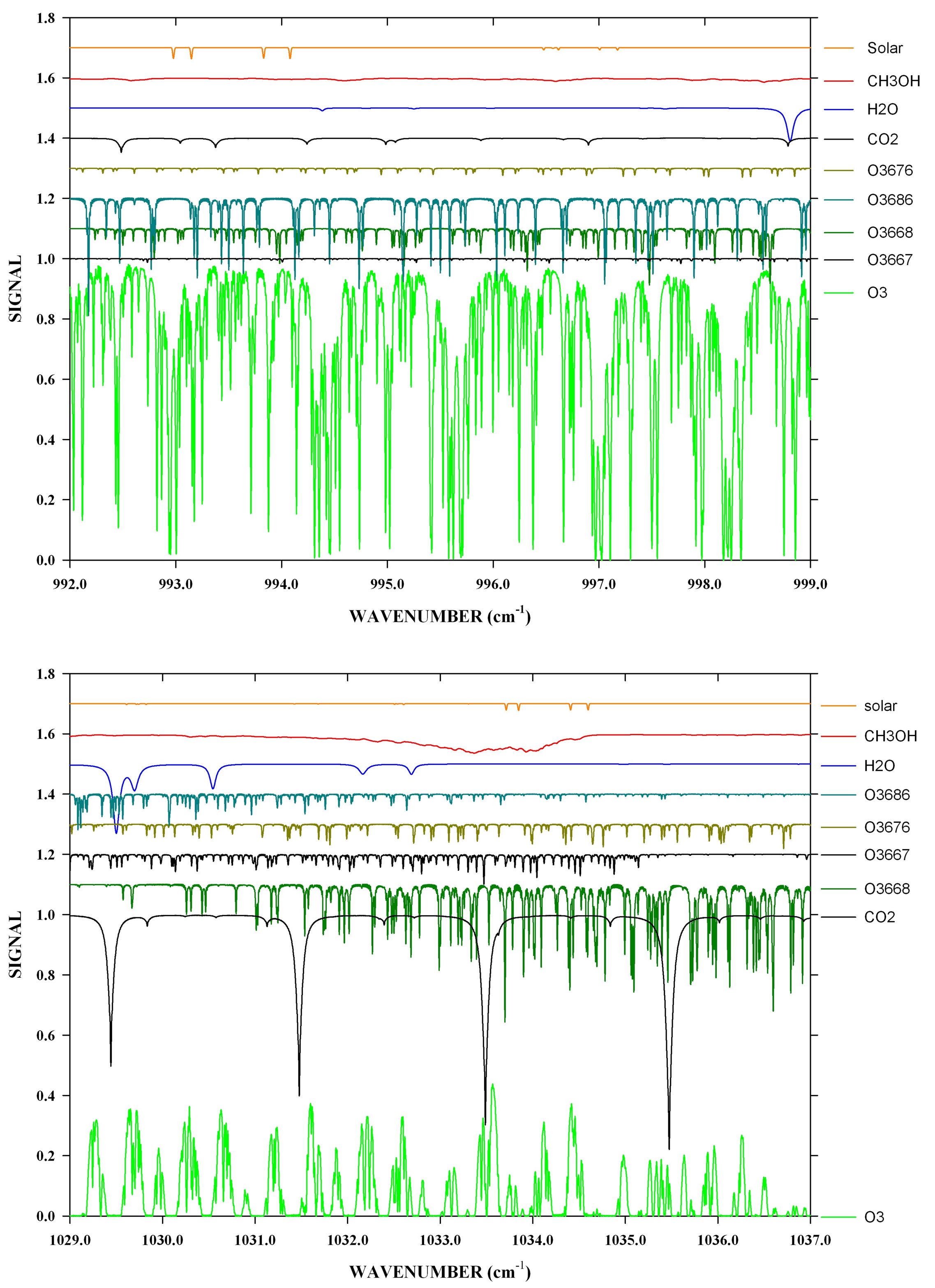

FIGURE 1

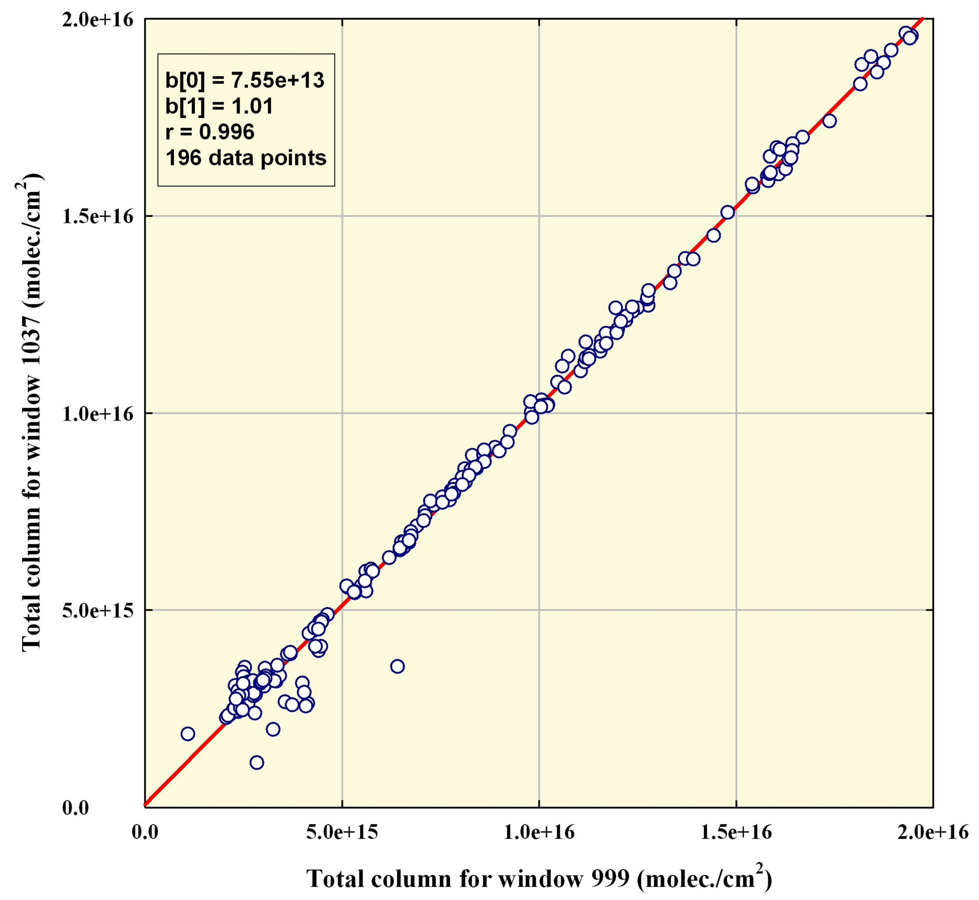

FIGURE 2

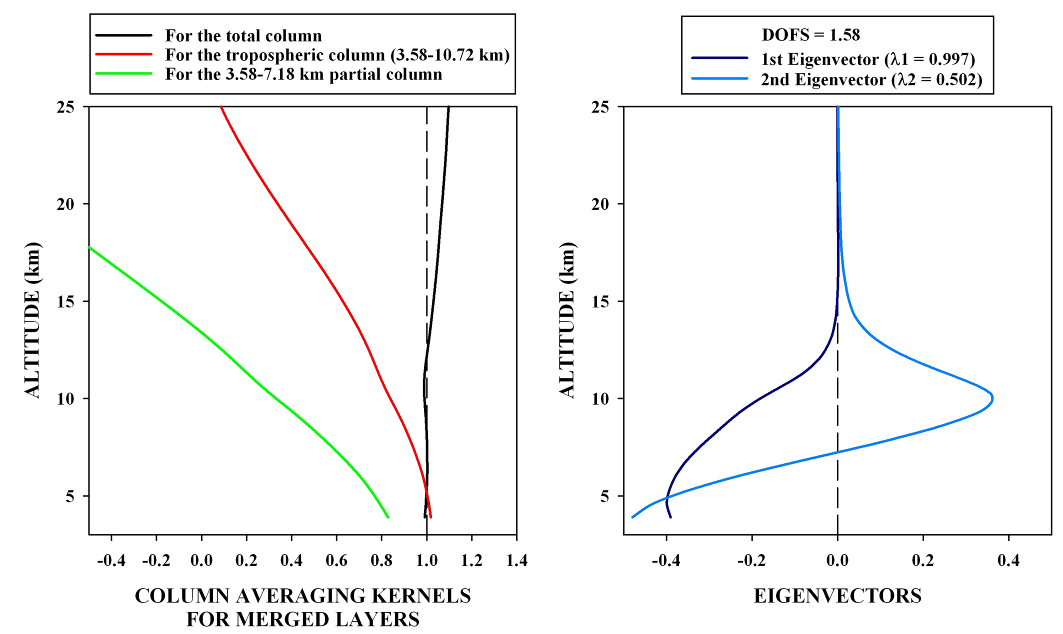

FIGURE 3

RETRIEVAL STRATEGY AND PRELIMINARY METHANOL TIME SERIES

-- Given the very good agreement found between the two candidate microwindows, we decided to combine them to maximize the information content. The adopted settings are as follows: (i) two spectral intervals ranging from 992 to 998.7 and from 1029 to 1037 cm^{-1} are simultaneously fitted, (ii) the vmr profiles of CH_3OH, O_3 and O3686 are retrieved during the iterative process while the a priori distributions of H_2O, CO_2, O3668, O3676 and O3667 are scaled, (iii) we adopted a 50%/km diagonal covariance and a Gaussian half width for interlayer correlation of 4 km for extra diagonal elements, (iv) since the fitting quality is significantly different in both windows, we selected two different values for the signal-to-noise for inversion, i.e. 170 and 40 for the 999 and 1037 domains, respectively. Line parameters from the HITRAN 2008 compilation were used while we assumed mid-day pressure and temperature profiles provided by the National Centers for Environmental Predictions (NCEP, see http://www.ncep.noaa.gov). Resulting typical information content is illustrated in **FIGURE 3**, the mean Degree Of Freedom for Signal (DOFS) amounts to 1.6 (instead of ~1.2 for the single window approaches). The retrieval is essentially sensitive to the troposphere, with limited vertical resolution (second Eigenvalue close to 0.5). Typical uncertainty on the total columns -including the smoothing error component- is of 7%.

-- **FIGURE 4** reproduces the daily mean total column time series of CH_3OH above Jungfraujoch, normalised to 654 hPa. Among striking features, we see a strong seasonal modulation with minimum values in December to February and maximum columns in June-August. The ratio between the lowest and highest individual columns exceeds 14. No significant long-term trend emerges from this 7-year long data set, and extension of our investigations is mandatory to verify this preliminary conclusion.

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