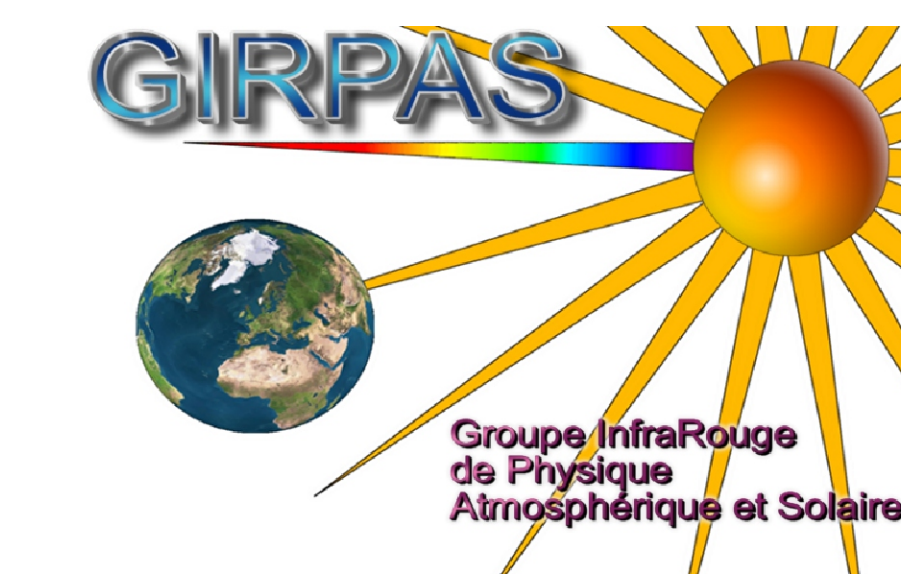


FIRST RETRIEVALS of METHYL CHLORIDE (CH₃Cl) from GROUND-BASED HIGH-RESOLUTION FTIR SOLAR OBSERVATIONS

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1. INSTRUMENTATION, 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, 46.5°N, 8.0°E, 3580m a.s.l.), within the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, <http://www.ndacc.org>).
- For the present investigations, we use high-resolution (0.003 and 0.005 cm⁻¹) IR solar absorption spectra, they have been recorded year-round, on a regular basis, with a Bruker IFS-120HR instrument, essentially since the early 1990s. Signal-to-noise ratios are larger than 1000, reaching 3500-4000 in the most favorable cases.
- All retrievals have been performed with the SFIT-2 algorithm (v3.91) which is based on a semi-empirical implementation of the Optimal Estimation Method formalism of Rodgers [1990]. This code allows in most cases to determine information on the vertical distribution of the species accessible to the ground-based FTIR technique. Here however, we only performed scaling of the methyl chloride (CH₃Cl) vertical distribution, given the weakness of the available spectral features. A priori profiles for the target and interfering species correspond to averages of WACCM model outputs for the 1970-2020 time period [the Whole Atmosphere Community Climate Model, <http://waccm.acd.ucar.edu>].

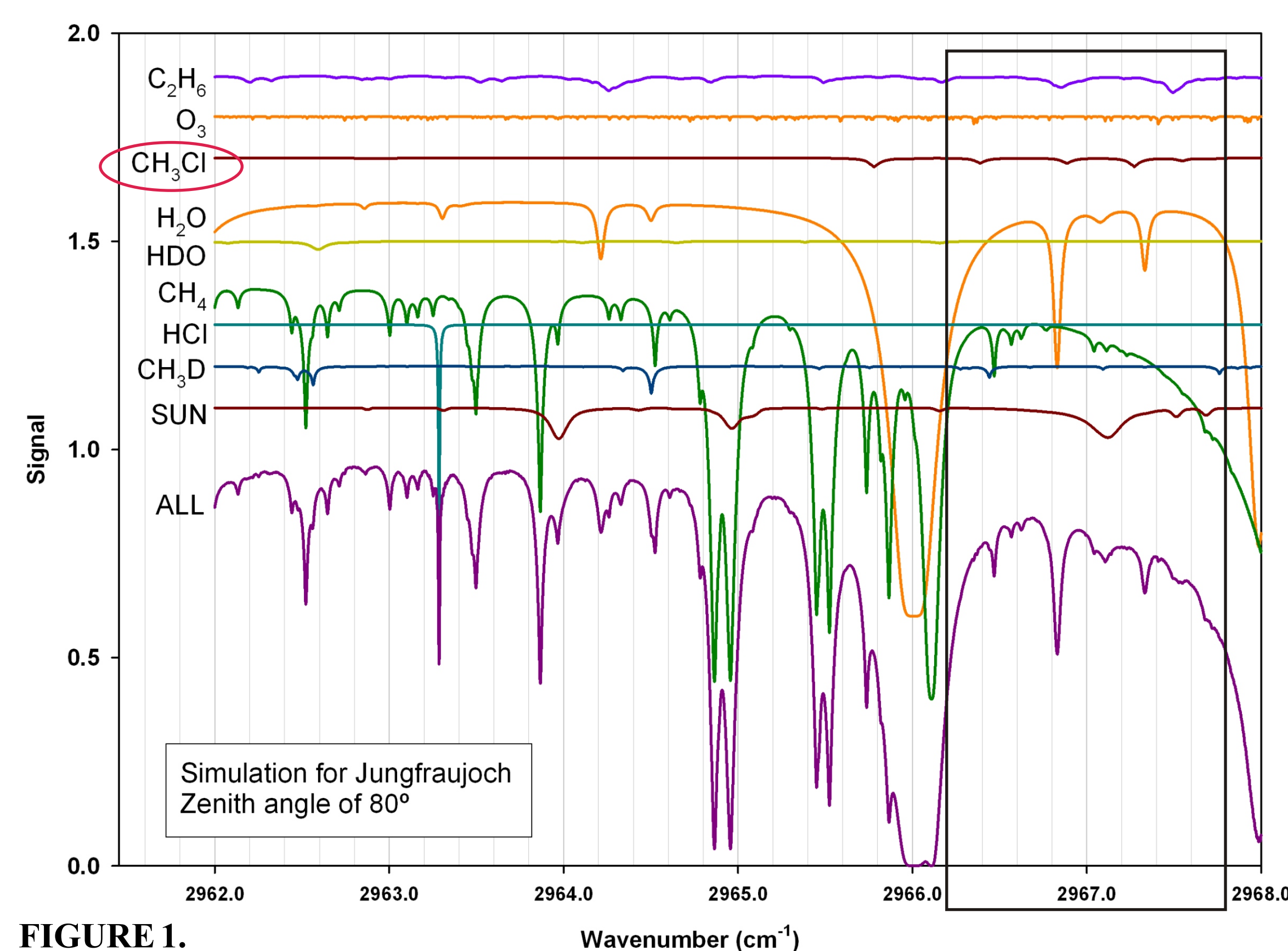


FIGURE 1.

2. THE CH₃Cl MICROWINDOW NEAR 3 MICRON

- FIGURE 1 displays a simulated absorption spectrum for the 2961-2968 cm⁻¹ region, encompassing weak absorption features of methyl chloride. The combined and individual absorptions are reproduced using different color codes, they have been shifted vertically for clarity. Identification of the absorbing gases is provided on the left hand side.
- This simulation was performed for the Jungfraujoch altitude (3.58 km), with a spectral resolution of 0.003 cm⁻¹ and an apparent zenith angle of 80°.
- For most gases, the HITRAN 2004 [Rothman et al., 2005] line parameters including the August 2006 updates have been adopted. For C₂H₆ however, the recent cross sections of Harrison et al [2010] have been used, after conversion to pseudolines by one of us [G.C.T.].
- It is obvious from FIGURE 1 that the retrieval of CH₃Cl from the ground is very challenging, with its 5 weak features (third trace from top, from about 2965.7 to 2967.5 cm⁻¹) located near (or below) strong interferences of methane and water vapor. In addition, weaker but numerous absorptions of e.g. C₂H₆, O₃, CH₃D or of solar lines further add to the complexity.
- It is important to notice that many CH₃Cl features are missing from current HITRAN compilations, in particular, Pacific Northwest National Laboratory (PNNL) spectra reveal that four additional absorptions occur from 2962 to 2965 cm⁻¹, i.e. in the less saturated part of the microwindow, where water vapor interferences are minimum.

BACKGROUND INFORMATION ON METHYL CHLORIDE (CH₃Cl)

- Methyl chloride (CH₃Cl) is one of the most abundant chlorine-bearing gas in the Earth's atmosphere and a significant contributor to the organic chlorine budget.
- Time series of in situ surface measurements indicate a mean volume mixing ratio of 550 pptv, with a significant seasonal modulation of 80 pptv (i.e. ~15%), peak to peak [Simmonds et al., 2004]. This species exhibits significant inter-annual variability, but no long-term trend.
- Major sources are from tropical and sub-tropical plants and dead leaves, oceans and biomass burning.
- The largest sink is oxidation by the hydroxyl radical, followed by soil uptake.
- Although balanced, its atmospheric budget is still affected by significant uncertainties, and contributions from unidentified sources and sinks cannot be ruled out. The estimated CH₃Cl lifetime is 1 year.

3. IMPROVEMENTS OF THE FITTING RESIDUALS THANKS TO THE NEW C₂H₆ CROSS-SECTIONS

- Although ethane is a weak absorber in the spectral domain under investigation (see FIGURE 1), it complicates the retrievals of CH₃Cl. Indeed, in some cases, the absorptions of these two species overlap. In addition, numerous C₂H₆ features were missing in the HITRAN compilations, even in the latest release [Rothman et al., 2009].
- Fortunately, new cross-sections for ethane in the 3 μm regions have been recently recorded at the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory [Harrison et al., 2010]. They were calibrated in intensity by using reference low-resolution spectra from the PNNL IR database. These improved cross-sections were recently released as an HITRAN update (see <http://www.hitran.com>).

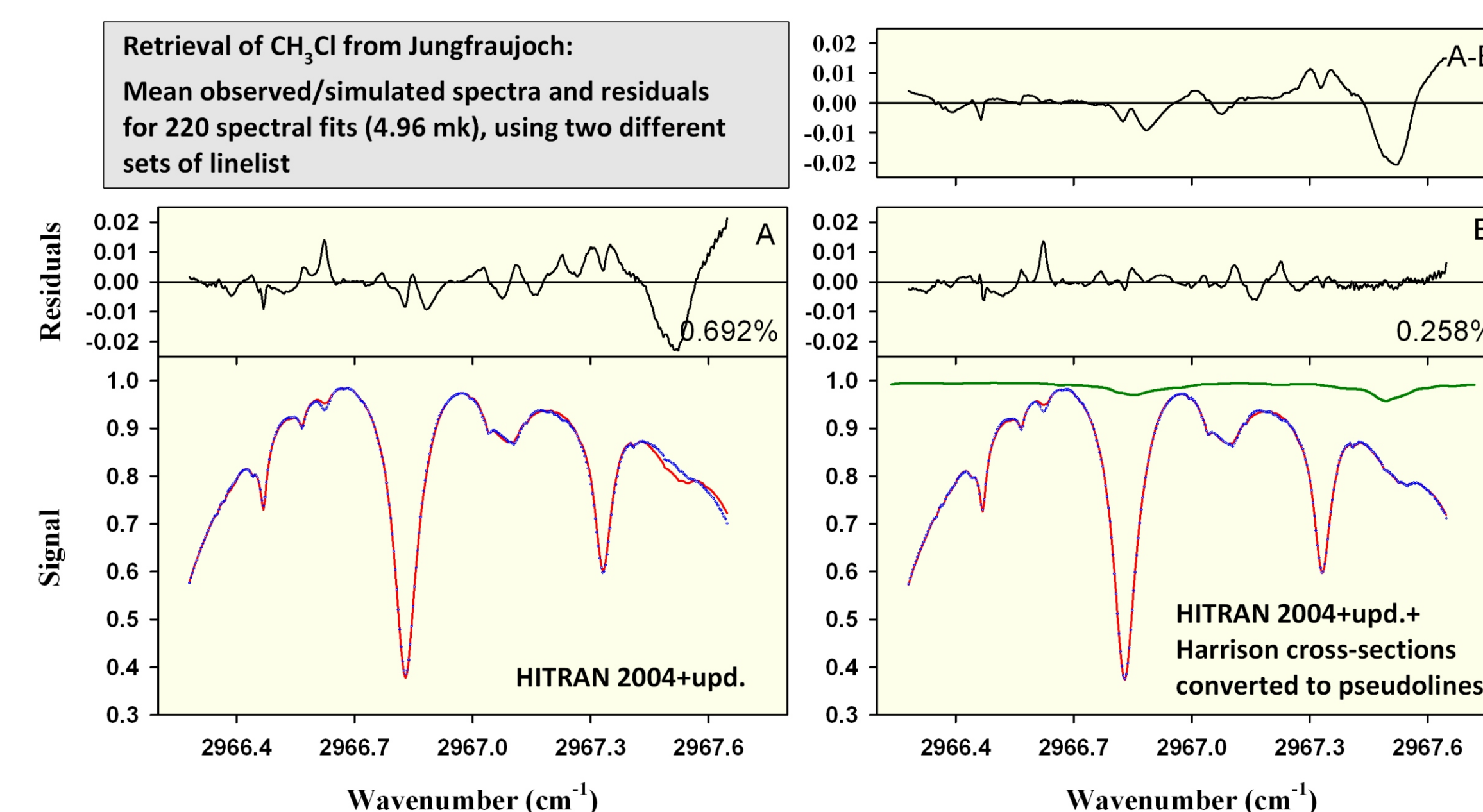


FIGURE 2. A series of 220 Jungfraujoch spectra have been fitted in a narrower range than shown in the simulation (see rectangle in FIGURE 1), focusing on the zone where line parameters are available for CH₃Cl. The retrievals were performed with two different line lists. For the left frame, the standard HITRAN 2004 edition including the August 2006 updates was adopted. For the right frame, the same set was used after substitution of the initial C₂H₆ line parameters with the pseudolines based on the Harrison et al. [2010] cross-sections. The green trace on the right frame shows the simulated ethane spectrum when adopting these new parameters. The mean observed and simulated spectra are reproduced in blue and red, respectively. Corresponding mean residuals are shown in frame A and B. The improvement resulting from the adoption of the new ethane parameters is obvious, with the root-sum-square of the residuals nearly divided by three (from 0.692 to 0.258%).

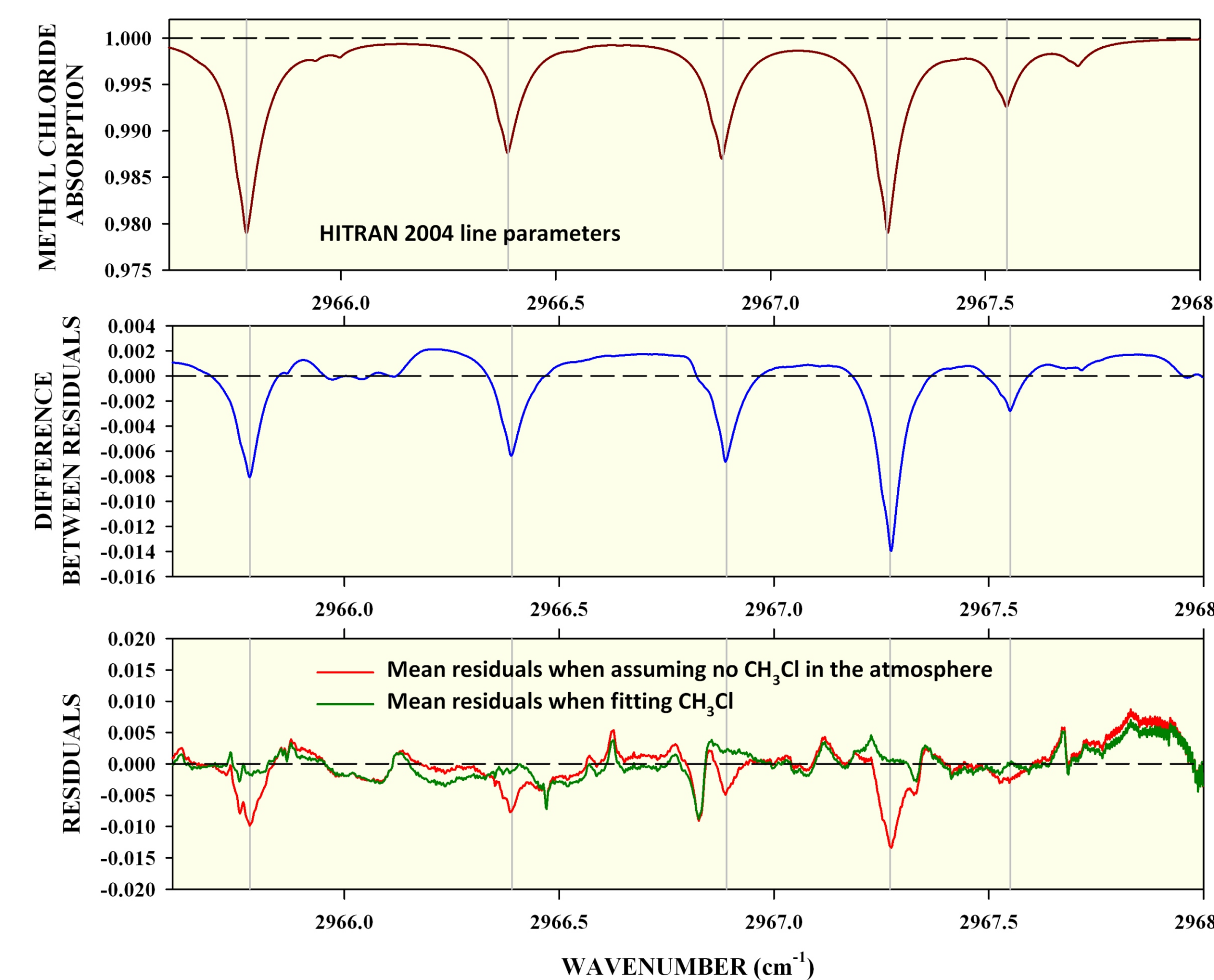


FIGURE 3. In order to detect methyl chloride absorption features in ground-based infrared solar spectra, we have successively fitted a subset of 16 Jungfraujoch observations (resolution of 0.003 cm⁻¹, from various seasons and with zenith angles of ~70°) by assuming no CH₃Cl in the atmosphere, or by adopting the WACCM a priori profile. Mean resulting residuals are shown in the lower part of FIGURE 3 (in red: no CH₃Cl, in green: CH₃Cl fitted), vertical grey lines denote the most obvious differences between the two averages. In the central frame, the difference between the green and red residuals is shown, further highlighting systematic features present when neglecting atmospheric CH₃Cl. Comparison with the simulated spectrum of methyl chloride reproduced in the upper frame indicate a good agreement and demonstrates that CH₃Cl can indeed be detected in high-quality and high-resolution ground-based spectra recorded at high altitude. A closer look at the comparison suggests that the relative strength of the feature at 2965.8 cm⁻¹ might be too large in HITRAN 2004.

4. CONCLUSIONS AND PERSPECTIVES

- A large subset of Jungfraujoch spectra has been fitted in the spectral range shown in FIGURE 2, to retrieve total columns of CH₃Cl. Interferences by the solar spectrum, by telluric H₂¹⁶O, H₂¹⁸O, H₂¹⁷O, CH₄, CH₃D, C₂H₆ and O₃ have been accounted for. The mean total column derived from the resulting timeseries is equal to 1.05 x 10¹⁶ molec./cm², i.e. significantly larger than the a priori value of ~0.7 x 10¹⁶ molec./cm². Another obvious feature of this first data set is the strong seasonal modulation characterized by maximum columns in August, minimum columns in February and a peak-to-peak amplitude of 25%. These first results are not in line with expectations, with a seasonal signal out of phase (in situ measurements indicate a maximum concentration of CH₃Cl in February) and an amplitude which appears too large. This could be due to the impact of an interfering gas, in particular water vapor, which shows maximum columns in August. It will therefore be necessary to refine the retrieval strategy, in order to minimize the impact of the interfering species on the CH₃Cl column. Possible options include e.g. setting up a two-step approach or considering only the driest days.
- The adoption of the recent Harrison et al [2010] ethane line parameters has clearly resulted in a significant improvement of the fitting quality in the vicinity of the 3 μm CH₃Cl absorption features, augmenting our chance to retrieve this species from remote sensing ground-based observations. There remains however place for improvement, for CH₃Cl for which numerous lines are missing in HITRAN, but also for methane. It is in particular unfortunate to notice the degradation of the fitting residuals when adopting the latest HITRAN 2008 compilation, which questions the quality of the new methane line parameters included in this more recent edition.

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