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Retrieval of ethane from ground-based FTIR solar spectra using improved spectroscopy: Recent burden increase above Jungfraujoch

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ABSTRACT

An improved spectroscopy is used to implement and optimize the retrieval strategy of ethane (C_2H_6) from ground-based Fourier Transform Infrared (FTIR) solar spectra recorded at the high-altitude station of Jungfraujoch (Swiss Alps, 46.5°N, 8.0°E, 3580 m a.s.l.). The improved spectroscopic parameters include C_2H_6 pseudo-lines in the 2720–3100 cm^{-1} range and updated line parameters for methyl chloride and ozone. These improved spectroscopic parameters allow for substantial reduction of the fitting residuals as well as enhanced information content. They also contribute to limiting oscillations responsible for ungeophysical negative mixing ratio profiles. This strategy has been successfully applied to the Jungfraujoch solar spectra available from 1994 onwards. The resulting time series is compared with C_2H_6 total columns simulated by the state-of-the-art chemical transport model GEOS-Chem. Despite very consistent seasonal cycles between both data sets, a negative systematic bias relative to the FTIR observations suggests that C_2H_6 emissions are underestimated in the current inventories implemented in GEOS-Chem. Finally, C_2H_6 trends are derived from the FTIR time series, revealing a statistically-significant sharp increase of the C_2H_6 burden in the remote atmosphere above Jungfraujoch since 2009. Evaluating cause of this change in the C_2H_6 burden, which may be related to the recent massive growth of shale gas exploitation in North America, is of primary importance for atmospheric composition and air quality in the Northern Hemisphere.

1. Introduction

Ethane (C_2H_6) is the most abundant non-methane hydrocarbon in the Earth's atmosphere with a lifetime of approximately 2 months [1]. On a global scale, the main

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sources of C_2H_6 are leakage from the production, transport of natural gas loss (62%), biofuel consumption (20%) and biomass burning (18%), mainly located in the Northern Hemisphere [1–3]. Biogenic and oceanic sources are generally very small [1]. The main sink of C_2H_6 in the troposphere is oxidation via reaction with hydroxyl radicals (OH), while in the stratosphere reaction with chlorine atoms dominates [4].

Ethane has a large impact on tropospheric composition and impacts the distribution of ozone (O_3) through several pathways, making it a compound of great interest as a sensitive indicator of tropospheric pollution and transport [5]. By acting as a major sink for tropospheric OH, the abundance of C_2H_6 impacts the lifetime of methane (CH_4). Thus C_2H_6 is an indirect greenhouse gas with a net global warming potential of 5.5 (100-year horizon; [6]). Similarly, C_2H_6 influences the atmospheric content of carbon monoxide (CO; [4]). Ethane also has a significant impact on air quality as it is an important source of peroxyacetyl nitrate (PAN), a thermally unstable reservoir for nitrogen oxide radicals (NO_x; [1,7]). By providing the main NO_x source in many regions of the atmosphere, PAN has a major effect on the production and loss of O_3.

Atmospheric C_2H_6 abundances can be measured using various techniques. Previous measurements of C_2H_6 include Fourier Transform InfraRed (FTIR) spectrometer observations by the balloon-borne Jet Propulsion Laboratory MkIV Interferometer [8], aircraft air samples collected during the NASA's Global Tropospheric Experiment Field Missions Pacific Exploratory Mission (e.g., PEM-West A; [9] and TRACE-A; [10,11]), solar occultations recorded by the Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS; [12]), ground-based measurements by gas chromatograph (e.g., [13–15]) and finally limb-scans performed by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) onboard the European ENVIronmental SATellite (ENVISAT; [16]). Analysis of these data records has significantly increased our understanding of the long range transport of C_2H_6.

Ethane has also been measured by ground-based FTIR technique at several latitudes in both hemispheres, covering different time periods (e.g., [5,17–25]). Nevertheless, strong latitudinal, seasonal and local fluctuations on small spatial and temporal scales make C_2H_6 secular trend determination difficult from the existing observations. Indeed, its concentration in the atmosphere is largely influenced by strong vertical mixing and dilution with background air during transport from emission sources.

In this paper, we present a 20-year long-term time series of C_2H_6 derived from ground-based high-resolution infrared solar spectra recorded with a Bruker 120HR FTIR spectrometer operated under clear sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (referred to below as ISSJ; Swiss Alps, 46.5°N, 8.0°E, 3580 m a.s.l.; [26]). Such a long-term time series in the remote atmosphere allows for air quality monitoring and provides a valuable tool for model and satellite validation. The solar spectra used here have been recorded within the framework of the Network for Detection of Atmospheric Composition Change monitoring activities (NDACC; see http://www.ndacc.org).

This work furthers the C_2H_6 dataset previously published in [19] and [27] for the ISSJ station and it presents an improved retrieval strategy in terms of reduced residuals and enhanced information content, combining three spectral domains for the first time at ISSJ. A careful selection of the available spectroscopic datasets is performed in order to minimize the fitting residuals. A thorough discussion of the retrieval strategy and data characterization (information content and error budget) is presented here along with trend analysis and preliminary comparison with the three-dimensional state-of-the-art global chemical transport model (CTM) GEOS-Chem.

This paper is organized as follows. A detailed description of the optimized retrieval strategy is given in Section 2. Section 3 reports the characterization of the FTIR geophysical products and provides a detailed error budget. Supporting model simulations are described in Section 4. Section 5 presents a preliminary comparison between FTIR and GEOS-Chem seasonal cycles of the C_2H_6 burden above Jungfraujoch as well as the entire 1994–2014 time series of daily-mean total columns and corresponding trends. Section 6 concludes this study with a short summary and discussions of the results, identifying avenues for future work.

2. FTIR data set

2.1. Instrumental setup

All the spectra analyzed here have been recorded at ISSJ, located in the Swiss Alps at 3580 m altitude on the saddle between the Jungfrau (4158 m a.s.l.) and the Mönch (4107 m a.s.l.) summits. This station offers excellent conditions to perform solar observations, particularly in the infrared, because of weak local pollution (no major industries within 20 km) and very high dryness thanks to the high-altitude and the presence of the Aletsch Glacier. Indeed, the amount of water vapor (H_2O), a strong interference in the infrared, is at least 20 times lower than at the sea level. Due to these factors, the ISSJ station allows for investigating the atmospheric background conditions over central Europe and the mixing of air masses from planetary boundary layer and free troposphere (e.g., [28,29]).

Here we use observations performed with a commercial Bruker IFS120HR instrument [26]. This spectrometer, affiliated to the NDACC network since 1991, is equipped with HgCdTe and InSb cooled detectors covering the 650–4500 cm^{-1} region of the electromagnetic spectrum.

The Bruker observational database investigated in the present study consists of more than 11,500 spectra recorded between September 1994 and August 2014 with an optical filter covering the 2400–3100 cm^{-1} range encompassing the perpendicular ν_7 fundamental stretching band of C_2H_6. Spectral resolutions, defined as the reciprocal of twice the maximum optical path difference, alternate between 0.004 and 0.006 cm^{-1}. The signal-to-noise (S/N) ratio varies between 300 and 4500 (average spectra resulting from several successive individual Bruker scans, when solar zenith angles vary slowly). The optimization of