First retrievals of methane isotopologue, CH₃D, from FTIR ground-based observations

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**INTRODUCTION & MOTIVATION**

Atmospheric methane (CH₄), with a lifetime of 8-10 years, is the second most important anthropogenic greenhouse gas (radiation forcing of 0.7 ± 0.2 W m⁻²; RF of CH₄ in 2011: 1.68 ± 0.35 W m⁻²; Steuber et al., 2013). Approximately one-fifth of the increase in radiative forcing by human-linked greenhouse gases since 1750 is due to methane (Nisbet et al., 2014). Identified emission sources include anthropogenic (coal mining, oil and gas exploitation, rice cultures, domestic ruminant animals, biomass burning, and waste management) and natural contributions (wetlands, termites, methane hydrates and oceanic sediments). Due to its sinks, methane plays a role of regulator of hydroxyl radical (OH) and of ozone precursor in the stratosphere (Montzka et al., 2011) while in the stratosphere, it acts as a source of water vapor and as a sink for chlorine atoms which reduces the rate of ozone depletion. Atmospheric methane concentrations have reached a new high at 1845 ± 2 ppb, accounting for an increase of 25% since pre-industrial times (WMO, 2016). In the last ten years, methane has been on the rise again at rates of ~0.3%/year (e.g., Bader et al., 2017), after a period of stabilization of about 5 years. This recent increase is not fully understood due to remaining uncertainties in the methane budget, influenced by numerous anthropogenic and natural emission sources. In order to examine the cause(s) of this increase, we focus on one of the main methane isotopologues, i.e., CH₃D. Methane isotopologues are emitted in the atmosphere with different ratio depending on the emission processes involved (Rigby et al., 2012). As heavier isotopologues will react more slowly than CH₄, each isotopologue will be depleted from the atmosphere at a specific rate depending on the removal process (Janssen et al., 2003). Methane isotopologues are therefore good tracers of the methane budget.

**INSTRUMENTATION & DATASET**

First development and optimization of the retrieval strategy for CH₃D from ground-based FTIR (Fourier Transform Infrared) solar observations with the SIFT-4 algorithm.

Toronto, ON, Canada (Wiacek, et al., 2007)

Bomem DA8 Fourier Transform Spectrometer
~240 days of spring observations at Eureka since 2004
Portable Atmospheric Research Interferometric Spectrometer for the InfraRed (~760 days of observations since July 2006)
Bruker IFS (~1430 days of observations since May 2002)

**A PRIORI MIXING RATIO PROFILES**

CH₄ vertical mixing ratio information is obtained from a Whole Atmosphere Community Climate Model (WACCM4.6, Marsh et al., 2013) simulation run as a stand-alone model with a resolution of 4°(latitude) x 1°(longitude) and 66 vertical levels (Buzan, et al., 2016). The model was run as a perpetual year 2000 for a total of 20 years of spin-up time followed by 3 years that were averaged to produce a single a priori mixing ratio profile per station. Water vapor mixing ratio profiles from daily averages NCEP reanalysis and ozone monthly averaged profiles over the years 1980-2020 from a WACCM simulation (WACCM) are used as a prior.

**SPECTROSCOPIC LINELISTS**

In order to minimize residuals, the best combination of available spectroscopic linelists has been determined: CH₄ and isotopologues
Spectroscopic list for GGG2014, TCCON data archive developed by Toon et al. (2014)
Experimental linelist of water vapor line parameters developed by Loss et al. (2017a and 2017b)

**RETRIEVAL CONSTRAINT**

The retrieval strategy is based on an altitude constrained Tikzon L₂ approach similar to the one recommended by the Network for the Detection of Atmospheric Composition Change for the retrieval strategy of CH₄.

The smoothing constrained is defined as:

\[ R = a \times \exp(-x^2) \]

where \( L \) is the constraint operator, \( x \) expresses the altitude constraint associated to the retrieval vertical grid, and \( a \) is the strength of the constraint. \( a \) is determined by minimizing the total error (measurement + smoothing error) as illustrated in Steck et al. (2002). Figure 1 illustrates the measurement and smoothing errors computed according to the formalism of Rodgers (1990) with respect to \( a \). The errors displayed in Fig. 1 are averaged errors over one year (2015) of retrievals from FTIR observations collected at Eureka.

**THE BENEFIT OF 4 WINDOWS (see Figure 2 for letter codes) 4**

Figure 3 illustrates the error budget (Bodges, 1990) depending on the use of 4 windows for both Toronto and Eureka measurements. Using 4 windows (A+B+C+D, in pink) allows us to simultaneously decrease measurement and smoothing errors while improving the Degrees of Freedom for Signal (DOFS) reaching a value as high as 1.43 (Toronto) and 3.95 (Eureka), see Fig. 6.

**WATER VAPOR SPECIFIC WINDOW ?**

In order to better identify the water vapor interference, a H₂O specific window (2941.65-2941.89 cm⁻¹; Bader et al., 2017) is tested as the fifth window.

**CH₄ PROFILE RETRIEVAL ?**

To assess isotopic ratios of CH₄ through H₂O computation, it is necessary to simultaneously retrieve pressure and accurate CH₄ total columns along with CH₄D. We observe a systematic bias between the retrieved and the archived CH₄ columns of approximately 11.2 and 11.5 % respectively with a scaled or retrieved CH₄ profile. Retracting the CH₄ profile increases smoothing, measurement and interference errors of about 0.02 %.

**ERROR BUDGET AND INFORMATION CONTENT**

Figure 6 illustrates averaging kernels, eigen vectors and associated eigen values for Eureka and Toronto, averaged over 2010 and 2015 and with DOFS of 1.43 and 3.95, respectively.

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Figure 3 - Illustrates the measurement and smoothing errors computed according to the formalism of Rodgers (1990) with respect to \( a \). The errors displayed in Fig. 1 are averaged errors over one year (2015) of retrievals from FTIR observations collected at Eureka.

Figure 2 - Averaged observed (in green) and calculated (in red) spectra (lower frame) as well as residuals in % (gray line in higher frame) derived from a representative set of observations (122 spectra) collected at Toronto during 2015. The individual contributions of each interfering gas have been vertically displaced for clarity. Window limits are (A) 2950.7 - 2951.1, (B) 3070.71 - 3073.15, (C) 3072.7 - 3073.15, (D) 2089.15 - 2089.9 cm⁻¹.