

Detections and Sensitive Upper Limits for Methane and Related Trace Gases on Mars during 2003-2014

Mumma, M.J.¹; Villanueva, G.L.^{1,2}; Novak, R. E.³ (michael.j.mumma@nasa.gov); ¹NASA Goddard Space Flight Center, ²Catholic University of America, ³Iona College.

Abstract: We present results from our comprehensive search for trace species on Mars, sampling multiple organic compounds (CH₄, CH₃OH, H₂CO, C₂H₆, C₂H₂, C₂H₄), hydroperoxyl (HO₂), three nitrogen compounds (N₂O, NH₃, HCN) and two chlorine species (HCl, CH₃Cl). Methane was searched on many dates and seasons and was detected at several locations on several dates. Most of these species cannot be detected with current space assets, owing to instrumental limitations (e.g., spectral resolving power).

Introduction: Searching for gaseous species on Mars is most favorable at Near InfraRed (NIR) wavelengths. The 2.8–3.7 μm range encompasses strong fundamental bands for many gases.

Detection limits improved significantly with the advent of extremely sensitive high-resolution infrared array spectrometers at large ground-based telescopes and advanced data analysis techniques, ultimately permitting our detections of methane (CH₄) in 2003 and 2005 [1]. The recent observations of methane by four groups [1-4] indicate regions of localized release, and high temporal variability. The principal plume of the release observed in 2003 contained ~19,000 metric tons of methane, with an estimated source strength ($\geq 0.6 \text{ kg s}^{-1}$, [1]) comparable to that of the massive hydrocarbon seep at Coal Oil Point (Santa Barbara, CA). By January 2006, the global abundance of methane represented only about 50% of the quantity released in March 2003 [1], suggesting its rapid destruction. Webster et al. [6] recently reported methane detections with TLS on Curiosity and found rapid modulation in its abundance.

In 2006, we collected 86,000 spectra (68,000 with CSHELL and 18,000 with NIRSPEC) and obtained global coverage. These observations were performed from January 6th to March 3rd (solar longitude L_s 352–22°), and we present data taken on January 6th 2006 with CSHELL and NIRSPEC over the same region where [7] recently reported detecting methane on Mars from observations taken on February 10th 2006. In the 2009–2010 period, we acquired ~400,000 Mars spectra during 27 observing runs (typically three nights per run) using three powerful high-resolution spectrometers (NIRSPEC at Keck II, CRRES at VLT and CSHELL at NASA-IRTF). From this period, we report results obtained from several representative datasets that span a broad range of seasons, Doppler shifts and spatial coverage, which only represent a fraction of the total search space. The datasets were mainly selected to provide the broadest seasonal coverage possible, but are

restricted in their spatial coverage, with a main focus on regions where methane releases were earlier observed.

Analysis: For the removal of telluric absorption features, we synthesize telluric spectra with radiative transfer models and adapt line intensities and spectral parameters from spectroscopic databases. The line intensities for each isotopologue in these databases are scaled from the isotopic ratios used in “standard” laboratory samples. For water the reference is VSMOW (Vienna Standard Mean Ocean Water), while for methane the carbon reference is VPDB (Vienna Pee Dee Belemnite). The isotopic composition of Earth’s atmosphere on the other hand differs greatly from these standards, and varies along the vertical column. The effect is particularly notable for deuterium depletion (δD) in water, dropping to –600‰ at the tropopause owing mainly to preferential condensation of HDO and subsequent rainout (Rayleigh fractionation, cf. [8, 9]). Until recently, no telluric radiative transfer model took this effect into account, and we were first to implement it for water [9].

The effect is more subtle for δ¹³C in methane. Tropospheric methane is depleted in ¹³C, with a typical value of –47‰ below 20 km owing to its biogenic origin, but its return towards smaller depletion at higher altitudes mainly arises from isotopic discrimination of methane reactions with Cl, OH and O(¹D) [10]. The recent claims of [5] when referring to the ground-based searches for methane on Mars by [1] are therefore surprising. In particular, [5] claimed that the ground-based detections of methane may be affected by problems with the treatment of the isotopic lines of methane (¹³CH₄). However, incomplete treatment of the telluric δ¹³CH₄ in the modeling of telluric spectra would have introduced emissions (not absorptions) in the spectra of [1] ([5] agrees with this view), further establishing the Martian detections. If not properly removed, terrestrial ¹³CH₄ signatures would appear on the blue wing in our spectra when Mars is red-shifted, but these are not seen (see Fig. S6 of [1]).

Results: Quantitative results will be presented.

References: [1] Mumma et al., Science 2009; [2] Formisano et al., Science 2004; [3] Krasnopolsky et al., Icarus 2004; [4] Fonti and Marzo, A&A 2010; [5] Zahnle et al., Icarus 2011; [6] Webster et al. Science Express 2014; [7] Krasnopolsky, Icarus 2012; [8] Moyer et al., GRL 1996; [9] Villanueva et al. JQSRT 2012; [10] Sugawara et al., GRL 1997.