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Laser Absorption Spectroscopy of Methane, Ethane and Methyl Mercaptan at The Cedars, a Mars Analog Site

Steve Vance, Lance E. Christensen, Christopher R. Webster, Keeyoon Sung
Jet Propulsion Laboratory, Caltech, Pasadena, USA (svance@jpl.nasa.gov / Fax: +01-818-393-4445)

Abstract

Methane (CH_4), ethane (C_2H_6) and methyl mercaptan (CH_3SH) are implicated in the origin of life at sites of low-temperature hydrothermal activity driven by serpentinization. Serpentinization may occur on Mars, in icy satellite oceans, and in other small wet bodies to a greater extent than on Earth, with important implications for life. We describe newly observed absorption features obtained in pure laboratory sample spectra of CH_3SH and C_2H_6 using the Carbon Isotope Laser Spectrometer (CILS), an infrared (3.27 μm) tunable diode laser spectrometer with capabilities nearly identical to those of the TLS instrument on the Mars Science Laboratory. The molecular species prove detectable by CILS and TLS at the sensitivities approaching the level of parts per trillion. These measurements demonstrate the capability for using ethane and methyl mercaptan, in combination with methane, as in-situ biosignatures for Earth-based and extraterrestrial exploration.

1. Introduction

Accumulated evidence suggests Mars was once habitable, and inhabited regions may exist in the present era if subsurface pockets of liquid water persist. The Mars Science Laboratory (Curiosity) is equipped with the Tunable Laser Spectrometer (TLS), which can sense isotopically depleted $^{13}CH_4$. Carbon-13 depletion of less than -60 per mil is well-established as an indicator of biological fractionation in methane-producing systems on Earth, but values of δ^{13}C between -30 and -60 per mil represent a grey area, in which methane may be produced by biological or abiological means (Webster, 2005). Recently, carbon-limited methanogens at the serpentinizing Lost City Hydrothermal Field have been shown to produce unfractionated methane (Bradley *et al.*, 2009).

Uncertainties in the reliability of δ^{13}C in methane as a biomarker could be addressed if additional biosignature features were detectable by TLS. Several species show absorption features in the 3-μm range, as seen in low-resolution FTS measurements[1]. Ethane and propane have recently been proven as biomarkers at sites of chemosynthesis on Earth (Hinrichs *et al.*, 2006). Volatile organic sulfur molecules oxidize rapidly in Earth's atmosphere, but may be useful for in situ measurements or for remote sensing of reduced exoplanet atmospheres. Pilcher (2003) describes the need for broadband (3-8 μm) spectroscopic characterization of two candidate biomarkers for life detection on exoplanets by telescopes on Earth (Domagal-Goldman *et al.*, 2010): methyl mercaptan (methanethiol; CH_3SH) and dimethyl sulfide (DMS; $(CH_3)_2S$).

2. Equipment and Methods

The Carbon Isotope Laser Spectrometer (CILS) is a field-deployable instrument that employs an interband cascade (IC) laser manufactured at JPL, with characteristics nearly identical to those of the methane-sensing laser on MSL (Webster, 2005). Custom-built hardware and electronics drive the laser and record absorption signals (Webster *et al.*, 1994).

Absorption features were observed in the pure sample spectra of methyl mercaptan recorded by CILS at 298 K using a custom-made 30.5 cm long glass cell with BaF_2 windows at sample pressures ranging from 0.5 to 5 kPa. The stated purity of the sample is 95%, purchased from Valley National Gas. We performed similar experiments using evaporated dimethyl sulfide, but no absorption signal of any kind was observed in CILS spectra.

Spectral band locations and relative line strengths of methyl mercaptan were confirmed by new Fourier transform spectra in the range 2200 - 3200 cm^{-1} , recorded at a resolution of 0.0045 cm^{-1} (unapodized) with a Bruker IFS-125HR Fourier Transform Spectrometer (FTS) at JPL (Sung *et al.*, 2009). Ethane was

[1] http://vpl.astro.washington.edu/sci/

observed in a 20.38 cm cold cell and observed at 130 K as well as at 298 K. Potentially corrosive methyl mercaptan samples was loaded into a 30.5 cm long cell at a pressure of 0.819 kPa (8.19 mbar) and placed inside the sample compartment of the FTS.

3. Results

For methyl mercaptan, more than 20 well-isolated (separated) rovibrational lines lines of varying strength are identified in both the CILS and FTS spectra at 3.27 μm, primarily from the ν_1 C-H stretch fundamental (Vance *et al.*, 2010).

The present measurements indicate that CILS (and TLS) can detect the molecule at the tens of parts per billion, well below the odor threshold for detection of 1 ppm.

The multitude of lines provide a means to estimate the relative mixing ratios for the various species even when some lines overlap. Methane isotope measurement is therefore possible even in the presence of other gases that may occur in natural settings on Mars or Earth.

Ethane and methyl mercaptan are stable under martian and terrestrial atmospheric conditions. Methyl mercaptan condenses at the lowest temperatures and highest pressures on both Earth and Mars, however, suggesting the possibility for concentration into low, cold, regions.

Laboratory analyses indicate methane and ethane are present in gas samples from The Cedars, a site of active serpentinization in northern California. Methyl mercaptan should also be present, but would have degraded to DMS or been oxidized to H_2S, H_2O and CO during storage. Another gas species, as-yet unidentified, is also present in spectra from the Cedars samples.

4. Summary and Conclusions

Our laboratory measurements show that CH_3SH and C_2H_6 have clearly separated rovibrational lines that allow high spectral resolution (and therefore high sensitivity) for detection at gas pressures typical of the atmosphere of Mars. This demonstrates the possibility for using these abundant molecules as an in-situ biosignatures for Earth-based and extraterrestrial exploration.

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