In Situ Detection of New Biosignatures On Mars And Earth: Laser Absorption features of Methyl Mercaptan (CH_3SH) at 3.27 μm.

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Methyl mercaptan (CH_3SH) is characterized in the 3.27 micron spectral region interrogated by the methane laser on NASA's Mars Science Laboratory rover. The compound is important in industry, in searches for biosignatures in the atmospheres of exoplanets and in studies of prebiotic chemistry. A related compound, dimethyl sulfide (CH_3SCH_3), showed no detectable signal even at high concentrations. Methyl mercaptan has multiple absorption features to either side of the C and H features already characterized for methane. Based on the present results, the Mars Science Laboratory can search for this CH_3SH when it reaches its destination in 2012.

Introduction

Simple microbial ecosystems are now known to thrive deep in Earth's crust in the absence of sunlight [1]. Life's earliest common ancestor appears to have been thermophillic, suggesting a deep origin on Earth, independent from the Sun. These insights provide impetus for searches for life on Mars and other locales in the Universe. Remote and in situ searches for extraterrestrial life require characterization of new biomarkers [2].

Biogenic methane is a major atmospheric constituent on Earth, and its presence in Earth's early atmosphere has been invoked as a solution to the faint-young-sun paradox [3]. Methane may also be produced abiotically, however, and isotopic measurements used to distinguish between the two sources can be ambiguous [2, 4, 5]. Methyl mercaptan has been suggested as a useful alternative. All known organisms on Earth use methionine for their metabolic cycles. As one of only two S-containing amino acids, the molecule's use should be anticipated in alternate biochemistries that may be employed by life on other planets. Breakdown of methionine generates the volatile gas methyl mercaptan, so this molecule can be expected as a universal bioproduct of metabolism. The production of mercaptan from a methanogenic community is estimated at one thousandth that of methane [2].

The present investigation suggests that The Tunable Laser Spectrometer (TLS), one of three instruments (QMS, GC, TLS) that comprise the Sample Acquisition Mission (SAM) on NASA's 2011 Mars Science Laboratory (MSL) should be capable of detecting methyl mercaptan. TLS has unprecedented capability for measuring methane, water and carbon dioxide abundances in the martian atmosphere and in gas evolved from heated soil samples. We characterized methyl mercaptan using a diode laser system comparable to the methane laser on TLS.

1 Equipment and Methods

CH4-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 [4]. Custom-built electronics excite the laser and detect and record resultant absorption signals. The hardware and software are similar to that described earlier in the context of airborne measurements [6].

Multiple measurements were made at 298 K and pressures ranging from 5 to 50 mbar in a pure (95 %) methyl mercaptan sample obtained from Valley National Gas, Inc, in coated transmission cell with a path length of 30 cm. Comparison measurements in pure (99 %) methane were made under the same conditions. We performed a similar survey using evaporated liquid dimethyl sulfide, but no absorption signal of any kind was observed.

2 Results

Laser absorption spectra for CH_3SH in the 3.27 μm spectral window interrogated by the Tunable Laser Spectrometer and CH4-CILS instruments show numerous features likely associated with the influence of the S on the C-H stretch in methane. Multiple features likely correspond to different isotopologues. Spectra for mercaptan and pure methane under the same conditions are shown in the main graphic and inset in Fig. 1.

References

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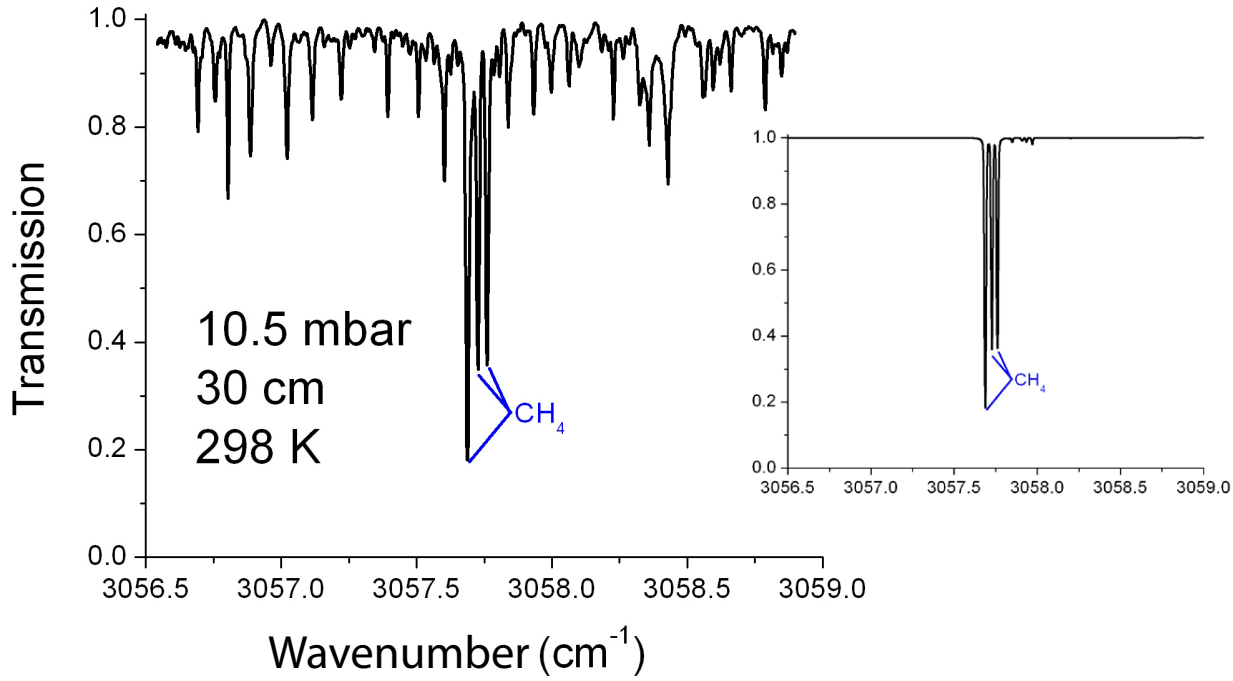

Figure 1: Laser absorption spectra for CH_3SH in the 3.27 μm spectral window interrogated by the Tunable Laser Spectrometer and CH4-CILS instruments developed at JPL show numerous features likely associated with the influence of the S on the C-H stretch in methane. Absorption spectra were measured at 25 ^{o}C and 10.5 mbar Spectra for pure methane under the same conditions are shown in the inset.

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