

TUNABLE LASER SPECTROMETERS FOR PLANETARY SCIENCE. C. R. Webster¹, G. J. Flesch¹, S. Forouhar¹, L. E. Christensen¹, R. Briggs¹, D. Keymeulen¹, J. Blacksberg¹, E. Alerstam¹, and P. R. Mahaffy², ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109; Chris.R.Webster@jpl.nasa.gov ²NASA Goddard Space Flight Center (GSFC), 8800 Greenbelt Rd., Greenbelt, Md., 20771. Paul.R.Mahaffy@nasa.gov

Introduction: Accompanying the development of lasers operating at room temperature, tunable laser spectrometer instruments have enjoyed a huge growth in capability for a wide range of applications in scientific research, medicine, industry, Earth and planetary space missions. Miniaturization has enabled the development of powerful new instruments for planetary missions to planets, satellites and primitive bodies and for the International Space Station (ISS) cabin monitoring.

The first atmospheric measurements were made in the 1980's [1] using the newly invented lead-salt tunable diode lasers that required liquid helium cooling and produced only a few microwatts of output power. The BLISS high-altitude balloon instrument weighed 1,500 kg and a single laser package (cryostat) weighed 70 kg. By the 1990's when liquid-nitrogen cooled lasers were available, several groups [2] from all over the world were flying tunable laser spectrometers on a wide variety of aircraft to understand Earth's ozone hole chemistry and dynamics. In the early 2000's with Quantum Cascade (QC) lasers available, the transition to room temperature operation began in earnest [3], so that by 2005 miniature laser spectrometers were being considered for planetary missions.

Today, room temperature QC, Interband Cascade (IC) and tunable diode lasers are available [4] over a large wavelength region, accessing molecules of interest to planetary science not just at the shorter near-IR wavelengths but also mid-IR wavelengths (Fig. 1) from HF (2.3 μm) to NH₃ (10 μm).

IR Tunable Laser Spectroscopy: Tunable laser spectrometers are uniquely suited to making high-precision gas abundance and stable isotope ratios because of their ability to scan at ultra-high resolution (0.0001 cm^{-1}) over targeted individual rovibrational spectral lines of the gas of interest without interferences that can be of concern with mass spectrometers.

For light molecules at pressures below ~ 100 mbar, IR tunable laser spectroscopy offers a direct, non-invasive, unambiguous method for measuring stable isotope ratios to sensitivities of $\sim 1\%$ for planetary low-mass (< 3 kg), all-solid-state instruments. Tunable laser spectrometers are well suited to H₂O, NO, NO₂, HNO₃, O₃, CO, CO₂, NH₃, SO₂, HCl, N₂O and CH₄.

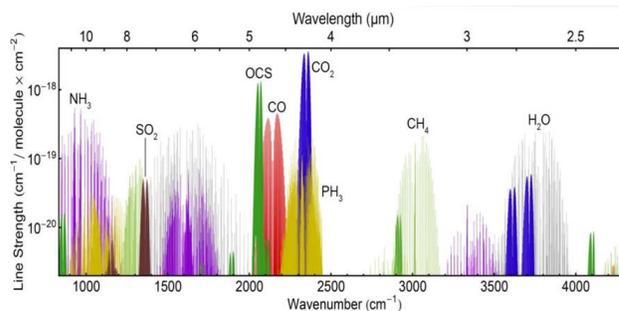


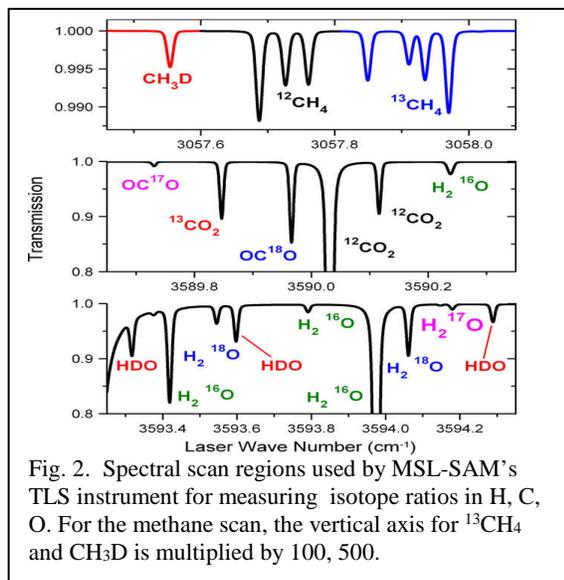
Fig. 1. IR bands of species of interest to planetary science, in particular for Venus, Saturn and Uranus.

Stable isotope ratios in C, H, N, O and S are powerful indicators of a wide variety of planetary geophysical processes that can identify origin, transport, temperature history, radiation exposure, atmospheric escape, environmental habitability and biology [5].

TLS in SAM on MSL's Curiosity Rover: The Tunable Laser Spectrometer (TLS) is one of three instruments that make up the Sample Analysis at Mars (SAM) suite [6] on the Curiosity rover.

During its' first three years in operation, TLS has determined the abundance of methane on Mars [7] and its variability at the Gale crater region, as will be updated during the workshop. In addition, both TLS and SAM's Quadrupole Mass Spectrometer (QMS) have measured atmospheric isotope ratios (see table with references [8, 9, 10, 11]) at unprecedented precision that in comparison with meteoritic data, tell a story of prolonged atmospheric escape that has been ongoing for nearly 4 billion years.

In addition to atmospheric measurements, TLS complements the SAM QMS in analyzing gases evolved from pyrolyzing rock samples acquired by Curiosity, at Rocknest [12], John Klein, and Cumberland sites. One important result [13] is measurement of the D/H in clays from Yellowknife bay. The low value of the measured D/H (~ 3 times SMOW) indicates that the mudstone was created significantly before much of the atmospheric escape occurred, and when Mars had a global equivalent layer of water of around 150 m.



TLS for Venus, Saturn, Titan and Uranus Probes:

In combination with the QMS, TLS is currently on strawman payloads for Discovery and New Frontiers missions that include atmospheric probes, for example for Venus, Saturn [14], Titan [15] and Uranus. In these applications in which a probe is descending very fast through the upper atmosphere, TLS will be upgraded with fast, agile digital electronics that drive several lasers simultaneously to maximize the data quality and return during these short but very important missions. Target gases include CO , OCS , H_2O , CO_2 , SO_2 , NH_3 and PH_3 (Fig. 1) and a variety of important isotope ratios. Requirements are typically 1-2% for D/H, and 2‰ for the triple isotopes in S.

TLS as a Combustion Monitor for ISS: In addition to developing TLS for future planetary missions, JPL is building a 5-channel TLS for the International Space Station (ISS) that will serve as a cabin monitor, providing detection of CO , HCN , HF , HCl , and CO_2 as an early warning system of possible fire hazards. For this application, NASA requires improved accuracy, response time and especially maintainability over existing electrochemical sensors.

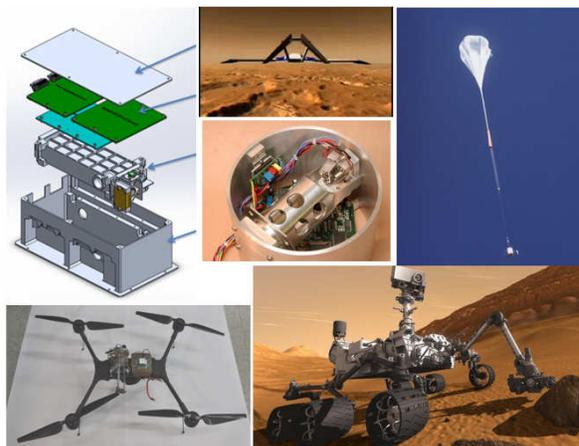


Fig. 3. Planetary tunable laser spectrometers in a variety of platforms: for CubeSats, Mars airplane, planetary probes, balloons, quadcopters and rovers.

We will review science results to date from TLS-SAM-MSL and also discuss laser spectrometers planned for future missions including the ExoMars lander.

References: [1] Webster C.R. and R.D. May, *J. Geophys. Res.* **92**, 11931-11950 (1987). [2] Webster C.R. et al., *Science* **261**, 1130-1134 (1993). [3] Webster C.R. et al., *Applied Optics*, **40**, 321-326, 2001. [4] Forouhar S. et al., *Appl. Phys. Lett.* **105** 051110 (2014) doi: 10.1063/1.4892655 [5] Criss R.E. (1999) *Principles of Stable Isotope Composition*, Oxford University Press, ISBN 0195117751; [6] P. R. Mahaffy, et al., *Space Science Rev.* **170**, 401 (2012). [7] C. R. Webster et al., *Science* **342**, 355 (2013). [8] S. Atreya et al. [9] Mahaffy P.R. et al., doi: 10.1126/science.1237966, *Science* **341**, 263 (2013) [10] Wong et al., *Geophys. Res. Lett.*; [11] C. R. Webster, et al., *Science* **341**, 260 (2013). [12] L. Leshin et al., *Science* **341**, (2013) DOI: 10.1126/Science.1238937. [13] P.R. Mahaffy et al., "The Deuterium to Hydrogen ratio in the Water that Formed the Yellowknife Bay Mudstones in Gale Crater", LPSC abstract 2014. [14] Mousis O. et al. IPPW 2013 Saturn poster [15] Webster C.R. et al., *Appl. Opt.* **29**, 907-917, (1990).

Acknowledgments: Part of the research described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA).