Highly Sensitive Tunable Diode Laser Spectrometers for *In Situ* Planetary Exploration

Ram Vasudev
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Dr.
Pasadena, CA 91109
818-354-5371
rvasudev@jpl.nasa.gov

Kamjou Mansour
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Dr.
Pasadena, CA 91109
818-354-7832
Kamjou.Mansour@jpl.nasa.gov

Christopher R. Webster
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Dr.
Pasadena, CA 91109
818-354-7478
Chris.R.Webster@jpl.nasa.gov

Abstract — **This paper describes highly sensitive tunable diode laser spectrometers suitable for *in situ* planetary exploration. The technology developed at JPL is based on wavelength modulated cavity enhanced absorption spectroscopy. It is capable of sensitively detecting chemical signatures of life through the abundance of biogenic molecules and their isotopic composition, and chemicals such as water necessary for habitats of life. The technology would be suitable for searching for biomarkers, extinct life, potential habitats of extant life, and signatures of ancient climates on Mars; and for detecting biomarkers, prebiotic chemicals and habitats of life in the outer Solar System. It would be useful for prospecting for water on the Moon and asteroids, and characterizing its isotopic composition. Deployment on the Moon could provide ground truth to the recent remote measurements and help to uncover precious records of the early bombardment history of the inner Solar System buried at the shadowed poles, and elucidate the mechanism for the generation of near-surface water in the illuminated regions. The technology would also be useful for detecting other volatile molecules in planetary atmospheres and subsurface reservoirs, isotopic characterization of planetary materials, and searching for signatures of extinct life preserved in solid matrices.**

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1. INTRODUCTION

The thrust of this work is the development highly sensitive tunable diode laser spectrometers for *in situ* planetary exploration, and for addressing the questions of whether life exists (or did it exist) elsewhere in other worlds and how life begins and evolves. The technology developed here is capable of sensitively detecting chemical signatures of life through the abundance of biogenic molecules containing carbon, hydrogen, oxygen and nitrogen, their isotopic composition, and chemicals necessary for habitats of life. It would also be useful for prospecting for volatiles such as water on the Moon and asteroids, and characterizing its isotopic composition.

The instruments described here are based on wavelength modulated (WM) cavity enhanced absorption spectroscopy (CEAS) using miniature distributed feedback (DFB) infrared tunable diode lasers (TDLs). This work represents a significant improvement over our feasibility studies described previously [1, 2]. The present setup is much more compact and the optical layout is more refined and robust. The very high sensitivity and compact instrument size in CEAS arise from the fact that it is possible to achieve very long pathlengths (few kilometers) despite the fact that the setup is quite short (few tens of centimeters). Long absorption pathlengths are obtained by trapping laser light in a confocal cavity containing the absorbing sample. The cavity is formed by highly reflective concave mirrors and the trapped light travels back and forth between the mirrors thousands of times while trickling out of the cavity. Thus an accumulated pathlength of a few kilometers is possible in a relatively short cavity.

Although long pathlengths are achievable in CEAS, a challenging issue is oscillations in the intensity of light exiting the cavity due to optical interference arising from overlap of laser light circulating within the cavity, thus compromising the signal-to-background ratio and hence the detection sensitivity. To reduce this effect, the light is injected off-axis into the cavity, thus reducing the laser beam overlap in the cavity. The residual oscillations are smoothed out further by using wavelength modulation (WM) techniques [3, 4]. This method allows us to use fairly small cavity mirrors (1.25-2.5 cm diameter), so a *multiple-species* spectrometer based on this approach would be small enough to be suitable for planetary applications. Typically, with current miniature DFB TDL technology, one cavity is required to detect one or sometimes two species of interest, so it is quite important to minimize as much as possible the size of each cavity in a multiple species instrument. In this respect, our approach is much more suitable than those using larger (5-10 cm diameter) mirrors. A multiple-species instrument based on such large mirrors would be quite unwieldy and thus may not be ideal for planetary applications due to severe space restrictions on *in situ* platforms that typically accommodate many instruments.

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Wavelength modulation also provides other well-known advantages [3, 4]. It is very effective in reducing the noise from the laser and detector, so it is possible to detect very weak absorption lines (especially minor isotopic lines). In addition, WM overcomes the issue of varying baseline slope commonly encountered in tunable diode laser spectroscopy arising from the fact that wavelength tuning is accomplished by varying the injection current applied to the laser, which also varies the laser output power. WM is especially suitable for use with diode lasers because they can be wavelength modulated by modulating the injection current.

We have developed two spectrometers based on WM-CEAS. The first one is a compact single-channel instrument for detecting water vapor in the near-infrared region. "Follow the water" has been a guiding principle for NASA missions because water is essential for existence of life as we know it and its detection is necessary in the search for habitable environments. Recent discoveries suggest an early warm wet climate on Mars under conditions in which life could have emerged [5, 6]. Presence of water in the sub-surface regions/glaciers at low latitudes has been inferred from the analysis of measurements from orbiters [7, 8] and by modeling [9-11]. Water-ice has also been found at the South Pole on Mars by the Phoenix lander [12]. Water has been detected on satellites in the outer solar system as well [5, 6, 13-14]. Of these, Enceladus and Europa are of special interest because they are the only objects in the outer Solar System that are suspected to harbor significant amounts of water, and thus could be habitable [15-17]. In addition to the detection of water, of considerable interest is the measurement of isotopic composition of water in various planetary reservoirs and attributing these to isotopic fractionation due to biological, geochemical and meteorological processes [5, 6, 18].

Water has also been discovered on the Moon. Orbiting lunar missions have revealed that the Moon is not bone-dry as once thought and water has been detected in the illuminated regions of the Moon [19-21], the shadowed poles [22-24] and nearby regions [24, 25]. Precise *in situ* location of water reservoirs would be of considerable importance to NASA's future human missions because water is essential for human survival. In addition, water can be electrolyzed to generate hydrogen and oxygen, which can be used as propellants. Characterization of lunar water deposits at the shadowed poles is also of scientific interest because they are thought to contain precious records of the early bombardment history of the inner Solar System that is available nowhere else [26]. *In situ* study of water (especially the isotopic composition) in the illuminated regions of the Moon is also of interest because it could help in elucidating the mechanism for generation of near-surface water.

Useful amount of water may also exist on asteroids [27-31]. This is especially relevant because of NASA's current interest in near-Earth asteroid-based Solar System exploration. Locating asteroid water reservoirs would be useful for astronaut survival and for generating ingredients for in-space propulsion. From a scientific viewpoint, the isotopic composition (especially the D/H ratio) of water on asteroids is of interest because it can be used to infer the relative distance from the Sun at which the asteroids were formed. Clearly, detection of water and its isotopologues by *in situ* instruments is of considerable interest to NASA's human and robotic space science programs.

The second prototype spectrometer that we are developing based on WM-CEAS is a multi-channel instrument for detecting an array of planetary volatiles, such as water, ammonia, carbon dioxide, carbon monoxide and methane.

2. EXPERIMENTAL

The single-channel water detection setup is shown schematically in Figure 1. It can be configured for detecting water vapor in the 1370 nm region or at 1880 nm. The output from a miniature tunable diode laser is collimated and injected in an off-axis manner into a confocal optical cavity formed by two highly reflective concave mirrors with 1 meter radius of curvature. The laser's wavelength is tuned over ≤0.35 nm (1.0 cm^{-1}) by applying a voltage ramp to a laser driver, which in turn applies a current ramp to the diode laser held at pre-selected temperatures attained with a miniature thermoelectric cooler. In the 1880 nm region, the combination of current and temperature tuning, allows us to cover absorption features in the 5314-5318 cm^{-1} range due to $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and HDO isotopologues of water contained in the cavity. In the 1370 nm region, we can tune in the 7292-7307 cm^{-1} range, covering absorption lines due to $H_2{}^{16}O$, $H_2{}^{18}O$ and HDO. The light exiting the cavity is collected and imaged onto a miniature InGaAs detector. The instrument is quite small ('shoebox' size), lightweight and consumes a few Watts of power while acquiring data. Figure 2 shows a photo of the spectrometer.

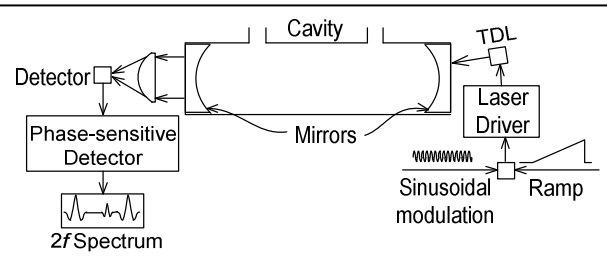

Figure 1 WM-CEAS setup (schematic). The wavelength of a tunable diode laser (TDL) is tuned by applying a current ramp to the laser and is simultaneously modulated by superimposing a sinusoidal current of a frequency f. The signal is monitored at twice the modulation frequency 2*f* (i.e., second harmonic detection). When combined with off-axis laser light injection to reduce beam overlap within the cavity, this results in excellent detection sensitivity for the sample contained in the cavity. Every absorption line in the 2*f* spectrum has the second derivative type line shape, as shown. For simplicity, light circulating in the cavity is not shown.

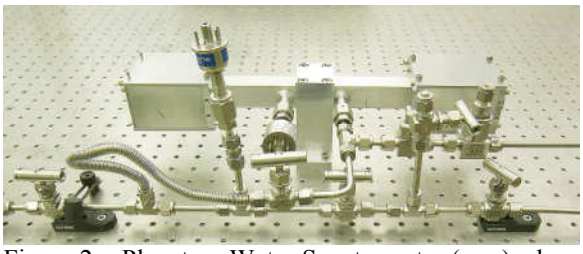

Figure 2 Planetary Water Spectrometer (rear), along with the sample handling lines in front. The sample handling system consists of several valves, a filter and a small vacuum pump.

The multi-channel prototype MW-CEAS instrument mentioned above consists of an array of four channels, each similar to the one described above.

2(a) Absorption Spectra

We record three types of absorption spectra, namely cavity transmission spectra with and without wavelength modulation, and wavelength modulated cavity enhanced absorption spectra. Cavity transmission spectra are acquired by monitoring the cavity output while tuning the laser wavelength by applying a voltage ramp to the laser driver. The small signal from the detector is amplified, averaged and then digitally smoothed. Wavelength modulated cavity transmission spectra are obtained by modulating the laser wavelength in addition to being tuned, by applying a small sinusoidal voltage at a suitable frequency *f* on top of the voltage ramp to the laser driver. The cavity output is amplified, averaged and digitally smoothed. In WM-CEAS, the modulated cavity output is processed with a phase-sensitive detector at twice the modulation frequency (2*f*), averaged and digitally smoothed. Each water absorption line in the 2*f* spectrum has a second-derivative type shape, as depicted in Figure 1.

2(b) Absorption pathlength

The absorption pathlength attained is determined by operating the diode laser in the pulsed mode by applying a current pulse to the laser (not shown in Figure 1) at a wavelength where water is transparent. The injected light travels back and forth between the cavity mirrors thousands of times and, at each reflection off the exit mirror, a small amount of pulsed light exits the cavity. Over a period of microseconds, the exiting light decays exponentially. Analysis of the decaying transient signal (so-called 'ring-down' transient) yields the pathlength achieved (see below).

2(c) Water Concentration

The water concentration in the cavity is determined by measuring the fractional absorption ($\Delta I/I_0$) in the cavity transmission spectrum without wavelength modulation and comparing it with simulations based on the HITRAN spectroscopic database [32], where ΔI is the amount of light absorbed due to a molecular absorption line and I_o is the cavity transmission without any absorption. The detection limit is obtained from the signal-to-noise ratio in the wavelength modulated (2*f*) spectrum.

3. RESULTS

Results from the single-channel water instrument operating at 1880 nm are described below, followed by a brief summary of preliminary results for few other planetary volatiles.

3(a) Absorption Pathlength

To characterize the sensitivity of the instrument, we first determine the absorption pathlength attained by using the laser in the pulsed mode at a suitable wavelength and measuring the transient cavity transmission, as described above. A typical ring-down transient signal is shown in Figure 3 for a mirror separation of 25 cm. The transient intensity as a function of time is given by

$$I(t) = I(t=0) \exp(-t/\tau) \qquad (1)$$

where I(t) is the intensity at a time t, $\tau = d/\{c\,|\ln(R)|\}$ is the $1/e$ (first order) decay constant, d is the separation between the cavity mirrors, c is the speed of light and R is the reflectivity of the cavity mirrors [1, 2]. An exponential fit to the ring-down signal shown in Figure 3 yields τ=14.4 μs, corresponding to R = 0.99994 and an absorption pathlength L of 4 km (L is defined as the distance traveled by light in time τ, i.e., $L=c/\tau$). This corresponds to ~17,000 traversals between the cavity mirrors. The absorption pathlength possible in cavity enhanced spectroscopy is typically ~100 times longer than in Herriott-cell based laser absorption spectrometers [33], with a correspondingly higher sensitivity.

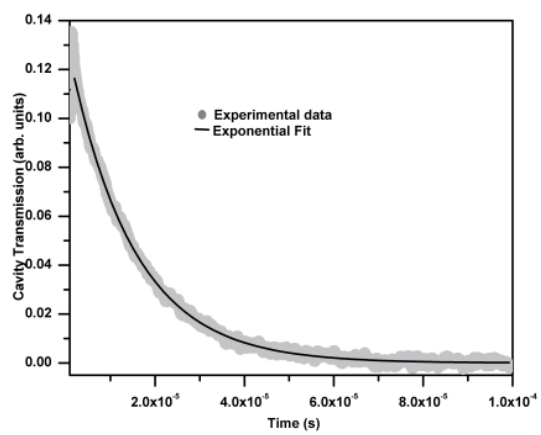

Figure 3 Transient cavity transmission ('ring-down' decay) obtained by using the laser in the pulsed mode at a wavelength where the sample is transparent. The spike near t=0 is due to radio frequency noise generated when the pulsed trigger source shuts off, and is not included in the fit.

3(b) Absorption Spectra and Detection Limits

(i) $H_2{}^{16}O$

The strongest $H_2{}^{16}O$ line sampled in this work is at 5316.235 cm^{-1} and allows us to detect water vapor in very small concentrations. Figure 4(a) shows the cavity transmission spectrum for this line without wavelength modulation. The oscillations are primarily due to detector noise and little due to residual interference effects. Also shown in (b) is the transmission spectrum with wavelength modulation, where the noise level is somewhat less. Both spectra have been subjected to signal averaging and digital smoothing. In contrast to the spectra in Figure 4, in our earlier work on water detection in the 1370 nm region the detector noise was less and the oscillations in the cavity transmission spectra was largely due to interference effects [1].

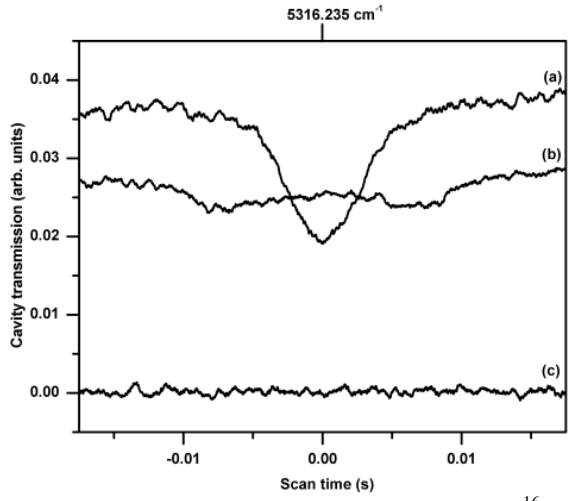

Figure 4 Cavity transmission spectrum of $H_2{}^{16}O$ at 5316.235 cm^{-1} (a) without wavelength modulation, signal averaging and smoothing; and (b) with wavelength modulation, averaging and smoothing. Trace (b) is displaced vertically for clarity. Trace (c) shows the background detector noise level.

The noise in the cavity transmission spectrum is readily suppressed by second harmonic (2*f*) detection, averaging and smoothing, as shown in Figure 5. Comparison with the transmission spectrum in Figure 4 shows that the enhancement in signal/noise ratio is quite significant. The noise, not noticeable on the scale of Figure 5, is ~1/11400 of the intensity at the line center (this is comparable to the enhancement attained previously for detection at 1370 nm [1]). With the observed fractional absorption ($\Delta I/I_o$) of ~0.47 (Figure 4), the noise level in the 2f spectrum corresponds to a fractional absorption 0.47/11400 ~ $4x10^{-5}$. The detection sensitivity, defined as three times this quantity, is ~1.2 x 10^{-4}.

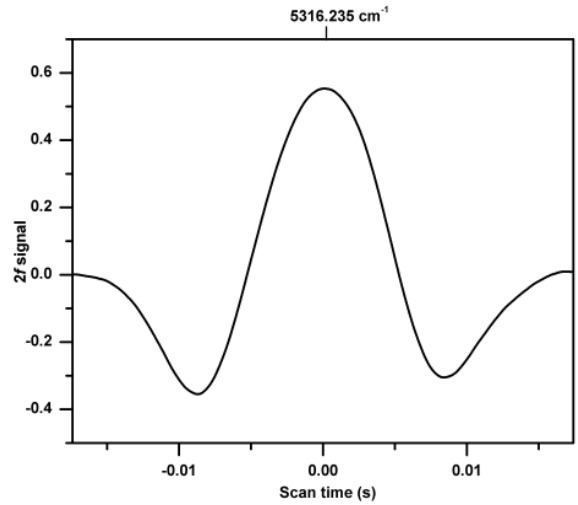

Figure 5 The second harmonic (2*f*) spectrum of $H_2{}^{16}O$ at 5316.235 cm^{-1}

To deduce the detection limit for water at 5316.235 cm^{-1}, we first obtain the sample pressure from the cavity transmission spectrum (Figure 4a) by using the HITRAN database [32] and calculating the fractional absorption given by

$$\Delta I(\nu)/I_0 = GA(\nu) / [1+GA(\nu)] \qquad (2),$$

where $A(\nu) = 1 - \exp[-\alpha(\nu)]$ is the single-pass fractional absorption at a frequency ν (i.e., the familiar Lambert-Beer law, where α(ν) is the single-pass optical depth), G = R/(1-R), and R is the mirror reflectivity determined above. The fractional absorption $A(\nu)$ is obtained from single-pass absorption spectrum simulated using the HIRTRAN database [32]. By comparing the observed fractional absorption (Figure 4) with HITRAN based simulations using equation (2), we obtain a sample pressure of ~5.8 x 10^{-4} mbar. With the detection sensitivity of 1.2 x 10^{-4} obtained previously from the 2f spectrum, the detection limit thus corresponds to 5.8 x 10^{-4} x 1.2 x 10^{-4} ≈ 7 x 10^{-8} mbar. We note that, if necessary, the detection sensitivity can be increased further by using a laser optimized for sampling the much stronger water line at 5327.390 cm^{-1} (~1878 nm), which is about an order of magnitude stronger. A detection limit of ~10^{-9} mbar will thus be possible. By comparison, the detection limit achievable is ~10^{-7} mbar at 1878 nm with Herriott cell-based spectroscopy [33]. We have used the 1880 nm region in the current work because of ready access to water isotopic lines.

(ii) Heavier Isotopologues of Water

We have also detected the heavier water isotopologues $H_2{}^{18}O$, HDO and $H_2{}^{17}O$. Figure 6 shows weak absorption lines due to $H_2{}^{18}O$ and HDO in the 5316.7 – 5317.1 cm^{-1} region, along with a stronger $H_2{}^{16}O$ line, at an estimated water pressure of ~$5x10^{-2}$ mbar. The detection sensitivity for the $H_2{}^{18}O$ line at 5316.745 cm^{-1} is ~$3x10^{-3}$, so the detection limit for this isotopologue is $5x10^{-2}$ x $3x10^{-3}$ x $H_2{}^{18}O$ abundance ($1.99x10^{-3}$) ≈ $3x10^{-7}$ mbar. For the HDO line at 5317.007 cm^{-1}, which is weaker, the detection sensitivity is

~$2x10^{-2}$, corresponding to an HDO detection limit of ~$1.8x10^{-8}$ mbar. We have also detected $H_2{}^{17}O$ at 5316.352 cm^{-1} (not shown here) at a detection limit of ~$7x10^{-8}$ mbar.

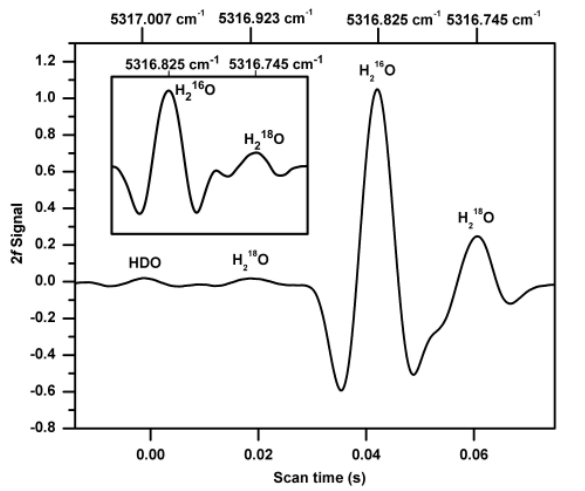

Figure 6 Second harmonic (2*f*) spectrum of water in the 5316.70 – 5317.06 cm^{-1} region. This is a relatively fast survey scan and the $H_2{}^{16}O$ and $H_2{}^{18}O$ lines at 5316.825 and 5316.745 cm^{-1}, respectively, are slightly overlapped. They are resolved in the slower scan shown in the inset. All line assignments in this paper are based on the HITRAN database [32].

(iii) Other Volatiles

We have also used WM-CEAS to detect ammonia, carbon dioxide, carbon monoxide and methane. Some of the initial results are shown here. Figure 7 shows the ammonia spectrum in the 1994 nm (5014 cm^{-1}) region, while Figure 8 shows the spectrum of carbon monoxide at 2379 nm (~4203 cm^{-1}). More details will be provided in future publications.

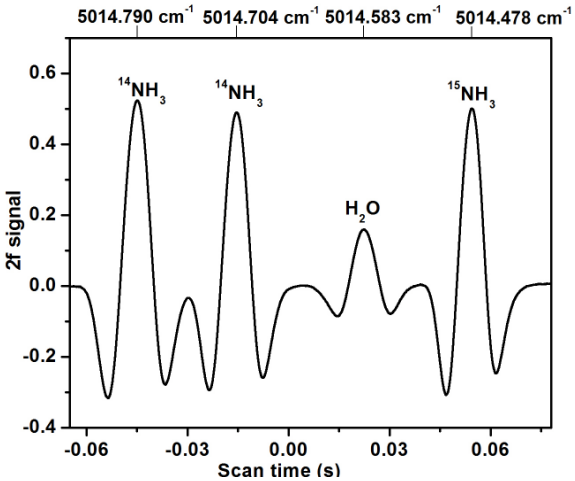

Figure 7 The second harmonic (2*f*) spectrum of ammonia in the 5014-5105 cm^{-1} region, showing absorption due to $^{14}NH_3$, $^{15}NH_3$ and $^{16}H_2O$.

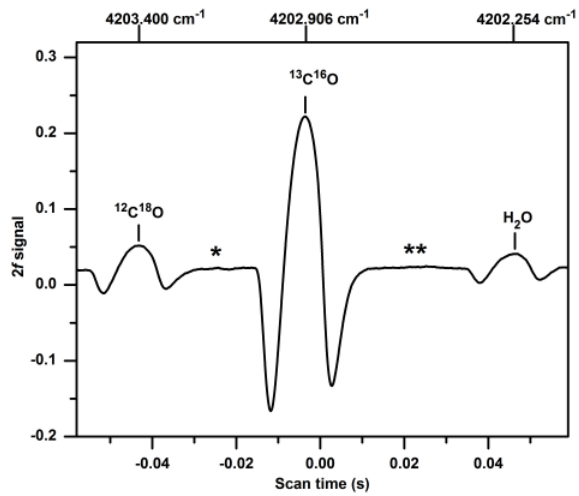

Figure 8 Absorption spectrum in the 4203 cm^{-1} region, showing lines due to $^{12}C^{18}O$ and $^{13}C^{16}O$ isotopologues, and $^{16}H_2O$. The features marked * and ** are due to very weak CO and water absorption lines.

4. PLANETARY APPLICATIONS

On Mars, laser spectroscopy would be useful for characterizing volatiles such as water in various reservoirs such as the atmosphere, subsurface regions/glaciers, aquifers, layered polar deposits, and in stratigraphy. Deployment of a laser spectrometer on Mars would also be useful for searching for records of ancient climate because climate change is accompanied by migration of volatiles such as water between various reservoirs. Climate change and volatile migration are significantly influenced by oscillations in the planet's obliquity over a period of millions of years because this is accompanied by regional temperature changes [9-11, 34]. During high obliquity there is increased summer time sublimation of water and other volatiles at the polar caps and deposition at lower latitudes. Since obliquity oscillates periodically, during the reverse process of decreasing obliquity the ice at lower latitudes sublimes and transfers back to the poles. Sublimation is relatively slow, so it is possible that some low-latitude regions with high albedo and low thermal inertia still retain some ancient volatile deposits in subsurface regions and glaciers, as suggested by the analysis of measurements by Mars orbiters [7, 8] and by modeling [9-11]. A key to understanding climate evolution is the accompanying change in the isotopic composition of volatiles (such as $^{18}O/^{16}O$ and D/H in water) in various reservoirs because the process by which each reservoir evolves fractionates the isotopologues differently and thus leaves a fingerprint on the isotope composition [35, 36]. Laser spectroscopy would be useful in this regard by providing measurements on water in the atmosphere as well as in in near- and sub-surface reservoirs/glaciers. For the latter measurements, we envision experiments involving extraction of ice cores and volatilization, followed by laser spectroscopy of the volatilized water vapor.

Missions to Enceladus would also benefit from laser spectroscopy, especially for characterizing the atmospheric, near-surface and subsurface chemical composition. Enceladus sports a cryovolcano that contains volatile molecules, with water being the predominant constituent [13]. The cryovolcano spews plumes into space from the geothermally heated south pole, so it may be possible to probe the subsurface chemistry through laser spectroscopy from an orbiter, i.e. without landing on the surface. Plumes have been observed on other geologically active moons such as Io and Triton, and have been speculated for Europa [5]. If present, characterization of Europa's purported subsurface ocean could be characterized by laser spectroscopy from orbit.

Laser spectroscopy would also be useful for confirming and substantiating the recent remote detection of water in the illuminated regions of the Moon, the permanently-shadowed poles and the nearby regions [19-25]. Characterization of water deposits at the lunar poles is of interest because it is thought to contain precious records of the early bombardment history of the inner Solar System that are available nowhere else [26]. Water and other volatiles play a significant role in the evolution of planets and their satellites, so the amount and the source (comets, for example) of the volatiles could be useful fingerprints for the evolutionary history. These parameters for water at the lunar poles can be obtained by laser spectroscopic analysis of water and its isotopologues, and could thus help us elucidate the history of the Earth-Moon system. Accessing water deposits in the permanently shadowed poles certainly poses significant technical challenges due to the absence of sunlight and very low temperatures [37]. Technologies for accessing the polar ice deposits are currently under development [38]. In the meantime, problems due to the absence of sunlight could be minimized by a careful choice of landing sites. As shown recently [39], there are a few sites along the rim of the Shakleton crater, for example, that receive glancing sunlight for most of the year and could be suitable for deploying landers and rovers. These regions are close to permanently shadowed regions containing trapped volatiles that are of considerable scientific interest and would be valuable for *in situ* resource utilization during future human missions. There are also permanently shadowed regions that are fairly shallow, so it might be possible to direct sunlight onto them with reflectors or periscopes and thus maintain rovers and scientific instruments at manageable temperatures. These regions could thus be suitable for *in situ* characterization of trapped lunar volatiles.

In situ measurements in the illuminated regions of the Moon could provide 'ground truth' for the remote measurements by the M^3 instrument on the Chandrayaan-1 mission [19] and by the HRI-IR and VIMS instruments during Cassini mission's lunar flyby *en route* to the outer solar system [20, 21]. This would also help us determine the isotopic composition of the water near the surface, which could help in elucidating the mechanism for generation of near-surface water. For example, a suggested mechanism involves the reaction of solar wind protons with oxygen-bearing minerals in the regolith. If this were the predominant mechanism for the production of the observed water, then the D/H ratio in the water may be expected to be similar to the D/H ratio ($\sim 2\times10^{-5}$) in the solar wind. If, on the other hand, the water was originally delivered by water-bearing comets and is now being exposed, then the D/H ratio should be similar to that in comets, which is much higher than in the solar wind.

For *in situ* exploration of lunar water, we envision a strategy that would entail identifying locations with possible subsurface water deposits, extracting a near/sub-surface sample at each location, volatilizing the sample in a miniature oven, followed by analysis by laser spectroscopy. For identifying promising locations, a laser spectrometer could be paired with a miniature neutron spectrometer (NS). In this scenario, an NS would be used on the same rover as the laser spectrometer for locating promising hydrogen-bearing sites. After zeroing in on these locations, laser spectroscopy would be used for a detailed analysis. This strategy could be implemented autonomously. An operational scenario we envision is akin to the Autonomous Science-craft Experiment (ASE) concept developed at JPL for Earth and planetary science missions [40]. The ASE concept uses on-board continuous planning, robust task and goal-oriented execution, model-based mode identification and recognition, and on-board machine learning and pattern recognition to increase science return by enabling intelligent down-linked selection and autonomous retargeting. Onboard algorithms detect 'trigger conditions' such as 'science events,' interesting features and change relative to previous observations. In one possible volatile detection/mapping scenario, a laser spectrometer would be paired up with an NS for target selection as mentioned previously, and a positive signal from NS (indicating a hydrogen-bearing deposit) would be used as a 'trigger condition' ('science event') to initiate sample acquisition and volatilization, followed by analysis of the volatilized water by laser spectroscopy. The rover with the dual instrument package could be used to systematically crisscross the lunar landscape ('lawn mower' style) and thus generate volatile distribution maps.

Laser spectroscopy would be useful for exploring asteroids as well. Asteroids were once thought to be devoid of much water because of their relative proximity to the sun, while comets were thought to be the water suppliers of the Solar System because they form farther out in space. This view has changed recently since the discovery of water and organics on the asteroid 24 Themis, possibly in subsurface reservoirs [27, 28], and on the asteroid 65 Cybele [29]. A recent study concludes that impacts due meteorites and their parent asteroids were the most likely sources of water on Earth [30]. Water has also been speculated to be present on the giant asteroid Vesta [31]. About half of Vesta is quite cold and receives very little sunlight, so water ice could have survived there for billions of years, possibly in the subsurface/near-surface region. Recent measurements by the

Dawn mission indicate the presence of hydrogen (possibly water) and other volatiles on Vesta.

The subsurface/near surface region could thus be a useful reservoir of water during human and robotic prospecting on asteroids. Locating water reservoirs would enable near-Earth asteroid-based large-scale exploration of the Solar System because water can be used to generate H_2 and O_2. These could be used for in-space propulsion, as described in NASA's Technology roadmap [41]. Such reservoirs would thus serve as Solar System 'fuel depots' and enable interplanetary travel. For prospecting for subsurface water during future asteroid missions, we envision a protocol in which samples are extracted from the subsurface, volatilized in a miniature oven and the evolved water vapor is analyzed by a laser spectrometer. Because of the instrument's high sensitivity, only a small sample of the regolith would be required for analysis.

Laser spectroscopic measurement of the isotopic composition of water-ice on asteroids is also of scientific interest. For example, from the D/H ratio of water, it is possible to infer the relative distance from the Sun at which the asteroids were formed. Asteroids formed farther out from the Sun tend to have higher deuterium abundance than objects formed closer to the Sun, and objects formed in the same regions should have a similar isotopic composition. Thus by comparing the deuterium abundance in water in carbonaceous asteroids to the deuterium in comets, it is possible to infer if they formed in similar reaches of the Solar System.

In addition to water, laser spectroscopy would be useful for sensitively detecting other volatiles in planetary atmospheres and subsurface reservoirs, characterizing planetary materials, and searching of signatures of extinct life preserved in solid matrices. The lack of organics and signatures of life at the Viking landing site has been attributed to the presence of reactive peroxides [42], so future searches will have to probe interior of solid materials that might be isolated from peroxides, such as polar subsurface ice matrices or interior of rocks. One of the possible signatures could be in the form of kerogen, which is a chemical residue left behind by the decay of microbes and preserved in sedimentary rocks. A possible probe for the presence of such signatures could be based on the fact that pyrolysis of terrestrial rocks containing kerogen (shale oil) yields ammonia [43], which could be detected and isotopically characterized by laser spectroscopy. The $^{14}N/^{15}N$ ratio in the NH_3 generated could be used to trace it back to kerogen's biological origin. Indeed "follow the nitrogen" has been proposed as a possible strategy for search for life on Mars and elsewhere [44]. Laser spectroscopy can also be used to detect signatures of life in the form of isotopic composition of nonequilibrium atmospheric species such as methane. A Herriot cell based laser spectrometer on board the Mars Science Laboratory is dedicated to precisely this goal [45].

Laser spectroscopy could also be used for characterizing the carbon content of planetary materials. For example, the CO and CO_2 detection capability could be used for characterization of kerogen type organic materials in rocks. We envision experiments to determine the carbon isotopic composition through stepped-combustion, followed by detection and isotopic analysis of the CO/CO_2 formed. The $^{13}C/^{12}C$ ratio in the products could be used to trace it back to kergoen's biological origin. Laser spectroscopy would also be useful for isotopic characterization of inorganic carbon such as carbonates through pyrolysis followed by the analysis of the CO_2 generated.

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BIOGRAPHIES

Ram Vasudev, Ph.D., is a research scientist at JPL. His interests include planetary laser spectrometer development, planetary chemistry, astrobiology, and chemical physics. He is also an avid nature photographer

Kamjou Mansour, Ph.D., is a member of the engineering staff at JPL. His interests include development of nanostructured materials for tunable lasers and fabrication of miniature lasers for planetary applications.

Chris Webster, Ph.D., is a program manager and senior scientist at JPL. His interests include development and deployment of planetary laser spectrometers. He is the lead scientist for the TLS instrument on the Mars Science Laboratory.