AEROSOL CAPTURE AND COMPOSITIONAL PROFILING OF VENUS ATMOSPHERE ON A DESCENT PROBE.

K. Simon[1], E. Eshelman[1], and P. Sobron[1]. [1]Impossible Sensing, St. Louis MO (ksimon@impossiblesensing.com).

Venus Atmospheric Characterization: The surface of Venus is shrouded by thick clouds, with a cloud deck that begins around 48 km altitude and has a ceiling 15-20 km higher. The clouds are made of microdroplets of sulfuric acid solutions with trace amounts of water. When observed in the visible range, the cloud layer appears as a featureless veil of white-yellowish hues. UV light, however, reveals a more dynamic and heterogenous layer with contrasting dark and bright patterns that grow and wane on timescales of a few minutes. Research since the 1978 Pioneer Venus mission suggests that the dark patterns in the clouds are due to one or more UV absorbing compounds [1]. Although strong astrobiological cases have been made theorizing the existence of a biological light absorbing pigment due to the presence of a habitable zone in Venus's atmosphere around 50 km, where pressures and temperatures are around 1 atm and 60ºC respectively, the true identities of the UV absorbers are unknown. To best characterize the atmospheric constituents in Venus's clouds as well as identify the unknown UV absorbers or detect traces of extant or extinct life, novel sample capture and measurement instrumentation is required. To meet these measurement needs, we are developing Venus Optofluidic Liquid TRap (VOLTR) as a subsystem that can discretely sample and measure aerosols and microdroplets in real-time through passive sample capture and subsequent high sensitivity surface-enhanced Raman spectroscopy (SERS) measurements during descent through the clouds of Venus (Figure 1).

VOLTR Innovation: VOLTR is a scientific payload that takes advantage of Raman spectroscopy instrumentation, considered a promising candidate for Venus atmospheric measurement and characterization [2], and enhances weak signals through high-sensitivity SERS measurements, enabling the detection and identification of atmospheric constituents present at trace levels. VOLTR consists of an aerosol trap that captures particles and passively samples microdroplets (< 10 µm diameter) during descent through the cloud layers of Venus. As the trap is made of SERS-active material with an ordered, nanostructured surface, *in-situ* SERS measurements can be performed immediately as sample adheres to the trap without the need for sample manipulation.

VOLTR utilizes a 515 nm pulsed laser to perform SERS measurements on sample adhered to the aerosol optical trap. The characteristics of the pulsed laser (variability in rep. rate and a high pulse energy) enable a unique self-cleaning procedure, which is a necessary innovation for discrete sampling/measurement compared to traditional SERS substrates which are single-use or have a limited lifetime.

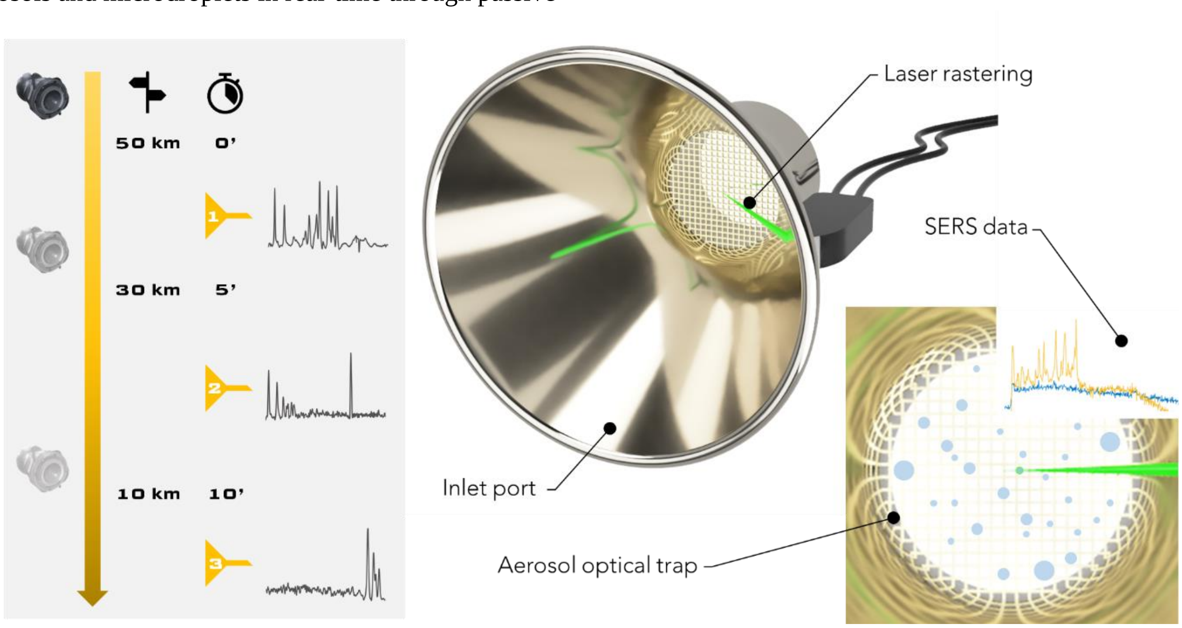

Figure 1. VOLTR concept of operation. As spacecraft or probe descends through the cloud deck, inlet funnels aerosols into an optical aerosol trap (< 10 mm diameter). The laser rasters the trap and conducts SERS measurements continuously throughout the duration of the mission. An in-situ cleaning method makes the trap reusable, enabling at least three discrete sampling and subsequent measurement events. SERS measurements enable high sensitivity (sub-ppm) detection and identification, through Raman spectral fingerprinting, of molecular functional groups and specific molecular identities.

As SERS measurements rely upon close spacing between the sample/analyte of interest and the nanotextured metal surface to enable constructive plasmon resonance that enhances weak Raman signals, once sample adheres to the SERS-active surface and is measured, traditional substrates are considered soiled as there are no more binding sites available for new sample interact with the surface. VOLTR, however, can immediately clean the SERS-active aerosol trap and remove small particles from the metal surface after a measurement by simply altering the laser parameters to fine-tune the energy density of the laser at the surface (Figure 2). The removal of sample from the trap through ablation and spot heating that occurs at high energy densities frees up the previously-occupied binding sites on the surface without damaging the trap, allowing for new sample to adhere to the SERS material. This cleaning procedure therefore allows the SERS-active trap to be recycled for multiple capture/measure/clean cycles such that analysis of the cloud structure can be performed multiple times during the probe's descent to Venus's surface.

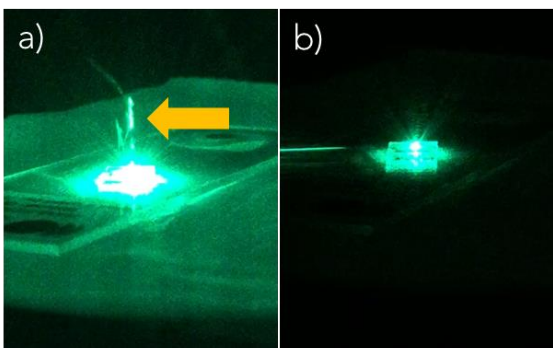

Figure 2. Demonstration of pulsed laser cleaning (a) compared with successful SERS measurement (b). VOLTR can rapidly switch between measurement and cleaning by altering the laser parameters to control the energy density at the SERS material surface.

The scientific outcomes of VOLTR are rapid, sensitive, and discrete characterizations of the composition of Venus's atmosphere through SERS measurements without the need for sample manipulation. VOLTR, therefore, will: (1) provide evidence relevant to the identification of the mysterious UV absorbers and potential organics or biosignatures indicative of extinct or extant life, (2) characterize the Venus atmosphere as a function of depth, and (3) enable the utilization of other measurement concepts through the passive sample of aerosol particles that can then be transferred on-board the descent probe for subsequent analysis (e.g. GC-MS), thus eliminating the need for a physical sampling mechanism or hardware.

VOLTR Performance: The aerosol optical trap is developed specifically to sample microdroplets of the size distribution present in Venus's atmosphere (from 0.3 to 8.0 µm mean diameter [3]). The physical properties of the trap are tailored to enable the capture of these particles while retaining the nanotexturing necessary to provide strong Raman signal enhancement.

Based on our team's preliminary results (Figure 3), VOLTR's expected performance is sub-ppm detection of organics and other trace compounds with a recycling capability enabling at least three reuses of the SERS-active surface.

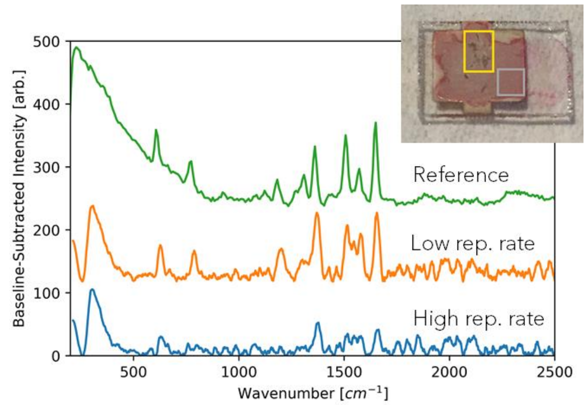

Figure 3. Example baseline-subtracted SERS spectrum on 10^{-4} M Rhodamine 6G standard using pulsed 515 nm laser compared to reference spectrum (acquired with 532 nm CW laser). Low rep. rate enables successful measurement while high rep. rate results in sample removal as indicated by reduced spectral intensity and loss of key peaks. Inset shows sample removal from high rep. rate (yellow box) compared to location of successful measurement at low rep. rate (gray box).

Significance: VOLTR addresses the need for high sensitivity compositional analysis of Venus's atmosphere while simultaneously demonstrating the potential to answer one of most intriguing scientific questions relating to planetary exploration and astrobiology: what is the mysterious UV absorber in Venus's atmosphere? VOLTR is a low-SWaP subsystem that can be configured for a variety of mission architectures to enhance the sensitivity of Raman instrumentation to trace compounds, organics, and biosignatures during aerosol capture or plume sampling.

References: [1] Limaye, S. S., Mogul, R., Smith, D. J., Ansari, A. H., Słowik, G. P., & Vaishampayan, P. (2018). Venus' spectral signatures and the potential for life in the clouds. Astrobiology, 18(9), 1181-1198.

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[3] Titov, D. V., Ignatiev, N. I., McGouldrick, K., Wilquet, V., & Wilson, C. F. (2018). Clouds and hazes of Venus. Space Science Reviews, 214(8), 126.