Deep UV Raman and Fluorescence Spectroscopy and Spatial/Spectral Imaging on Mars and on Earth

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Abstract: – 35 words

Deep UV Raman & fluorescence spectroscopy has emerged as an increasingly valuable active sensing tool for standoff detection and chem/bio multi/hyperspectral imaging of trace concentrations of materials on surfaces on Mars and on Earth.

Technical Summary of Presentation: 2-pages

1.0 Background

Over 20 years ago we began a quest to develop deep UV Raman and fluorescence instruments, taking advantage of the sensitivity, specificity, and other demonstrated benefits of these deep UV methods compared to near UV, visible, and IR methods, based on the work of Professors Sandy Asher of University of Pittsburg, Bill Nelson of the University of Rhode Island, and others. Our first goals were Raman detection of nucleic and aromatic amino acids for application to the emerging astrobiology needs for detection of trace amounts of materials of biological origin, whether extant or existing. This original quest was for detection of evidence of life on Mars, with the prospect of similar missions to Europa, Enceladus, Titan, and beyond. This quest resulted in the successful landing and operation of the first deep UV Raman and fluorescence spectrometer, called SHERLOC, on the Mars Perseverance Rover on February 18, 2021.

The original motivation was detection of trace organic materials imbedded in natural environmental substrates where many problems existed with sensitivity, specificity, fluorescence and ambient light interference, and other issues. The four primary benefits of deep UV excitation include:

a. Fluorescence-free Raman from targeted materials or other surrounding materials within the laser beam spot diameter. Associated with this is the reverse interference of strong Raman signals with weak fluorescence signals of trace amounts of single ring organics like phenylalanine and tyrosine as well as benzene, toluene, xylene, and other single or low ring organics.
b. Enables simultaneous detection of both Raman and ultra-sensitive fluorescence signals, providing orthogonal and complementary information about a target. Raman provide information about the chemical bonds while fluorescence provides information about the overall electronics configuration of an unknown material.
c. Enhanced Raman signal strength, especially for organics, due to resonance Raman effects.
d. Enables fluorescence detection of a nearly all organic materials no possible with excitation at longer wavelengths.

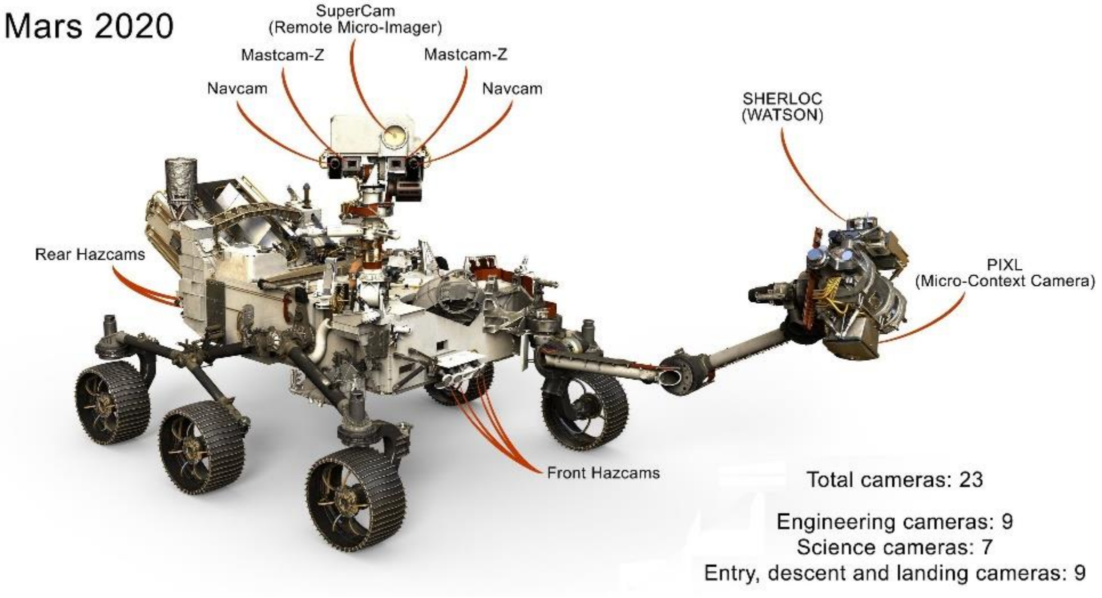
Along with these benefits are certain challenges, among which are the increased potential for damage of sample materials due to thermal and/or photochemical damage. Photochemical damage is typically the least of the damage mechanisms, even for delicate biological and organic materials. Thermal damage is often the major challenge, depending on the method of excitation of a sample. Limits of detection are normally dependent on the total excitation dose on a sample, or average power density times time. Thermal damage depends on dose rate, or peak power during a dose. Thermal damage limits the ability of miniature diode pumped solid state harmonic generated deep UV lasers. Excitation during pulse widths of a few nanoseconds can produce temperatures with a sample of many hundreds of degrees centigrade, causing instantaneous disruption to proteins, peptide, and other organic materials. An extreme example of this is laser breakdown spectroscopy (LIBS) where material with the laser beam spot size are brought to thousands of degrees centigrade, evaporating and ionizing all of the material in the laser beam spot. Balancing these effects is important to enable the important advantages of deep UV detection methods.

2.0 Mars Perseverance SHERLOC

The earliest NASA goals for Raman instruments for Mars were focused on visible to NIR based Raman instruments due to the emergence of miniature version of lasers at these wavelengths. Problems associated with fluorescence interference with Raman emissions limited observations specifically for materials containing organics and key minerals associated to aqueous alteration. In addition, visible and IR systems were challenged with interference from solar and stellar background illumination. Comparatively, the deep UV fluorescence/Raman mitigated fluorescence and ambient light background issues and increased sensitivity to organics.

Mars Perseverance landed on Mars on February 18, 2021 and is successfully generating 248 nm excited deep UV Raman and fluorescence spatial/spectral maps of trace and bulk material to this date. Two Raman instruments are on Perseverance: SHERLOC, the deep UV Raman and fluorescence spatial/spectral chemical imaging instrument and SuperCam, a combined standoff 532 nm time-gated Raman system plus 1064 nm LIBs. SHERLOC development had the unique challenge to adapt to the robotic arm, mass, and power consumption requirements and has led to the smallest integrated deep UV Raman & fluorescence spectrometer system. It also survives ambient temperatures from -135C to +70C without survival heaters or temperature regulation. An additional challenge for SHERLOC was to handle the shock and vibration loads of launch, landing, and operation on the surface of Mars.

There is a unique synergy between these two Raman instruments where Supercam's time-gating solution enables key mineral analysis while SHERLOC has a very high sensitivity to organics and enables high spatial resolution (100 µm) to assess the distribution of organics and aqueous altered minerals. Combined, these provide a new view to understand the geology and possible signs of life on Mars.



3.0 Back to Earth

Along the journey to Mars, we also developed other instruments with funding and collaboration with NASA, NSF, DOD, EPA, and other government and private organizations. Among them were several instruments developed for NASA for astrobiology analog missions to Antarctica, the Arctic, and deep Ocean to detect trace microbial materials in these environments. One of these instruments was the Deep Exploration Biosphere Investigative tool (DEBI-t), developed for NSF and University of Southern California, to detect and map microbial populations vertically along the walls of a 0.6 km deep ocean bottom bore-holes located about 4.5 km below the ocean surface at the Mid-Atlantic ridge. Another instrument was developed and used on many deep Ocean dives to investigate microbial material in an around deep Ocean vents.

We also developed instruments for DOD for standoff detection of chemical, biological, and explosives (CBE) materials which to detect and map CBE materials on surfaces at distances up to 5 m. These instruments include a DTRA and DHS sponsored Standoff Handheld CBE (SCBE) point-detection analyzer and a standoff CBE spatial/spectral mapping instrument (MAESTRO) for Defense Science & Technology Laboratory (DSTL) in United Kingdom.

We also developed instruments for industrial applications for process analytical measurement applications for the pharmaceutical, semiconductor, and other industries as well as for environmental testing and a wide range of R&D applications and environments.

4.0 Summary

We will describe the science and technology and many of the instrument developments in greater detail during our presentation at CLEO in May 2022.