

High-speed Pulsed Raman for Mapping of Minerals and Organics on a Microscopic Scale

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Overview: We present a miniaturized planetary surface instrument for *in situ* identification and quantification of minerals and organics, with surface mapping capabilities on a microscopic scale. We have previously demonstrated the benefits of time-resolved Raman spectroscopy using spectra obtained on planetary analogs [1]. Recent technological advances in the high-speed pulsed Raman (HiPuR) spectrometer presented here have enabled further expansion in capabilities, encompassing a much wider range of samples. For example, with HiPuR it is possible to obtain diagnostic Raman spectra from samples exhibiting a large interfering background from short-lifetime fluorescence as well as from samples traditionally sensitive to damage.

Introduction: The High-speed Pulsed Raman (HiPuR) instrument builds on the widely used 532 nm (green) laser Raman technique, but uses *time gating* to separate out pervasive background interference caused by fluorescence (from minerals and organics) resulting in unambiguous Raman spectra as illustrated in Fig. 1. This fluorescence rejection capability ensures that every point measurement making up a Raman map yields a diagnostic spectrum, unlike conventional methods where many spectra are unusable because of fluorescence [e.g. see ref. 2]. In addition to fluorescence rejection, time-gating also enables operation in daylight

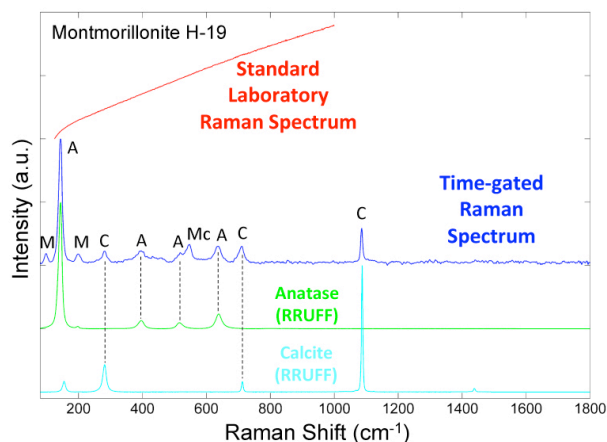


Figure 1. Time-gated Raman spectrum (dark blue) of a highly fluorescent phyllosilicate sample measured by our 1024 x 8 time-gated SPAD detector. Minerals identified are (M) montmorillonite, (A) anatase, (Mc) mica clay, and (C) calcite. This spectrum could not be obtained without time-gating as evidenced by the overwhelming fluorescence background visible in the standard laboratory Raman spectrum (shown in red with a different intensity scale for clarity).

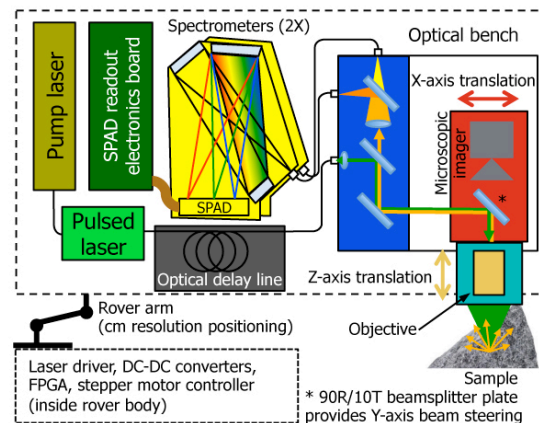


Figure 2. Block diagram of the prototype High-Speed Pulsed Raman Spectrometer.

conditions without the need for light shielding, an important factor, especially for power-constrained missions where measurements are only feasible during the warmer daylight hours.

Fig. 2 shows the overall instrument architecture as it would be mounted on a rover or lander arm. Modular design allows for straightforward adaptation to a broad range of missions with different accommodation requirements. The ability to perform high-speed pulsed Raman spectroscopy in a miniaturized arm-mounted package can be attributed to two key enabling technologies: a sub-ns time-gated single photon avalanche diode (SPAD) detector synchronized with a High-speed Microchip (HMC) laser capable of emitting ~ 100 ps pulses at repetition rates as high as several MHz. We focus in particular on the design of the HMC lasers currently under development, and their optimization with SPAD detectors.

Custom time-gated detectors: The high-speed pulsed Raman spectrometer relies on two custom time-gated 1024 x 8 pixel arrays of Single Photon Avalanche Diode (SPAD) arrays operated in single photon counting mode and capable of sub-ns time gating down to 700 ps [3], each paired with a spectrometer to cover the complete spectral range in Raman shift from ~ 100 cm^{-1} to 4000 cm^{-1} . Because the SPAD is a solid state detector, it offers a significant reduction in size, weight, power, and complexity when compared to traditional photocathode-based detectors such as streak cameras that have until now been the only technology available for achieving sub-ns time resolution. This

means that fast time-gating has now become feasible for planetary surface missions, offering the enhanced science return associated with fluorescence rejection and daylight rejection, with minimal added complexity.

The time-gating process is illustrated in Fig. 3. The detector collects returned light only during the time gate. In order to get the maximum benefit from fluorescence rejection, the detector and laser can be synchronized to line up the laser pulse near the falling edge of the detector gate. In that way, the time resolution of the instrument can be approximated as the laser pulse width.

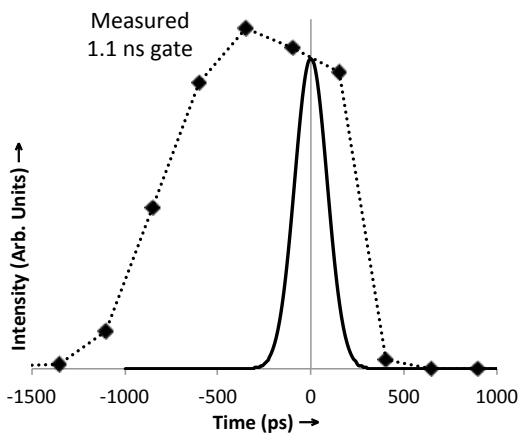


Figure 3. Illustration of the time-gating process shown for a 1.1 ns SPAD time gate and a 200 ps laser pulse. In the early gating scheme, the gate begins before the laser pulse in order to maximize fluorescence rejection. Note that the SPAD cannot produce an ideal rectangular gate, but rather has a 250 ps fall time which reduces the ultimate time resolution slightly.

High-speed microchip lasers: At the heart of our most recent advancement is the high-speed microchip (HMC) laser, a passively Q-switched diode-pumped solid state (DPSS) laser built in-house and based on a laser microchip from BATOP GmbH with a novel semiconductor saturable absorber [4-6]. This laser offers significant advantages over conventional passively Q-switched DPSS lasers, in particular shorter pulses, higher repetition rates, and electrically tunable output power. In this way we can improve the instrument sensitivity by increasing the repetition rate, which allows for lower peak power on the sample for any given average power. This means that the laser power on the sample can be increased without inducing sample damage. We can use the electrical tunability to adjust the power on the sample for optimal return. The narrower pulse width provides improved time resolution, beneficial for samples with short lifetime fluorescence.

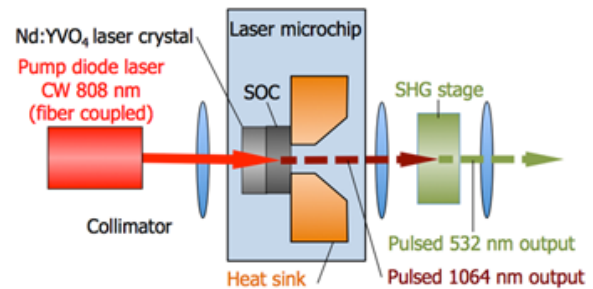


Figure 4. Laser architecture for the high-speed microchip laser.

Applications for future NASA missions: By combining capabilities for the identification of minerals present in geological materials, with capabilities to detect organic matter, laser Raman spectroscopy is a compelling technique for landed missions targeting rocky and icy bodies. Raman is non-destructive, requires no sample preparation, and is well suited for deployment on a lander or rover arm. In combination with micro-scale imaging, Raman can directly interrogate rocks and regolith materials, while placing compositional analyses within a microtextural context. The combination of these advantages of Raman spectroscopy combined with the fluorescence and daylight rejection capabilities of HiPuR makes this an ideal instrument for future robotic exploration of planetary surfaces at a wide range of Discovery, New Frontiers, and Flagship class mission destinations, including asteroids, comets, the Moon, Mars, Venus, Europa, and Titan.

References: [1] J. Blacksberg *et al.* (2016) *Applied Optics*, 55(4), 739-748. [2] Frosch *et al.* (2007), *Anal. Chem.* 79, p.1101 [3] Y. Maruyama *et al.* (2014) *IEEE JSSC*, 49 (1) [4] B. Bernard *et al.* (2014), *Proc. of SPIE* Vol. 8960 [5] E. Mehner *et al.* (2013) *Appl. Phys. B*, 112, 231-239 [6] A. Steinmetz *et al.* (2009), *Appl. Phys. B*, 97, 317-320

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