PERFORMANCE OF SUPERCAM'S REMOTE RAMAN SYSTEM AT JEZERO CRATER, MARS.

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Introduction: The Perseverance Rover on NASA's Mars 2020 Mission has been exploring Jezero crater since the rover landed on Mars on February 18, 2021. Among the science payload on the rover, there are two Raman spectroscopy systems deployed for the first time on another planet, SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals) and SuperCam. SHERLOC is a UV micro-Raman system with resolution of 43 cm^{-1}. It uses a deep UV laser source and is specially designed for detecting organic and luminescence from targets [1]. SuperCam is a suite of combined multiple analytical techniques including LIBS (laser induced breakdown spectroscopy), time-resolved Raman spectroscopy (TRRS), time-resolved luminescence spectroscopy (TRLS), visible and near-infrared spectroscopy, as well as a Remote Micro-Imager (RMI) and a microphone [2,3]. SuperCam includes a 1064/532-nm laser with a 4-ns pulse capable of operating at 3-10 Hz, acquiring several (up to 400) shots per analyzed spot. We have evaluated the performance of the SuperCam's remote Raman system on Mars by comparing its prelaunch performance using the Raman spectra of SuperCam Calibration Targets (SCCTs), as well as its ability to identify minerals and salts in situ at Jezero crater, Mars.

SuperCam is described in detail in previous publications by Wiens et al. [2] and Maurice et al [3]. In brief, SuperCam is composed of three main subsystems: the Body Unit (BU) is located inside the body of the rover and contains the three spectrometers used for LIBS, VIS Raman and luminescence, and UV-VIS reflectance measurements. The SuperCam Calibration Targets (SCCTs) assembly is located on the rover deck [4,5]. The spectrometers of SuperCam are calibrated for wavelength on a regular basis using the LIBS line from the SCCT titanium. The Raman shifts are calculated using the diamond Raman line, which is shifted by 1332 cm^{-1} from the exciting laser line at ~532-nm.

The 532-nm green laser beam produced in SuperCam's Mast Unit is expanded by a compact Galilean telescope, and with distance it remains a nearly collimated beam of 8.4 mm x 9.3 mm [3]. The field of view (FOV) of the SuperCam's spectroscopic system is 0.74 mrad [4]. Figure 1 illustrates the projection of the spectrometer FOV on the image of the 532-nm laser beam as a function of distance and temperature. In addition, the green laser beam has a few hot spots as shown in Fig. 1. The intensity and the wavelength of the 1064 nm laser oscillator is reported to have a slight temperature dependence [3].

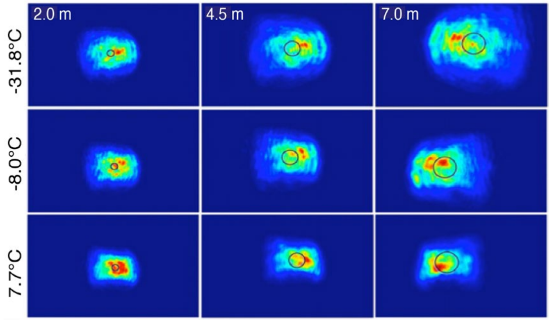

Figure 1. *Alignment of the green laser beam and the FOV of SuperCam's spectrometer system at various distances and at different temperatures. Laser intensity is shown as blue-green-red for increasing intensity, and black circles mark the spectrometer FOV [3].*

Results and Discussion: Figure 2 shows the Raman spectra of SCCT diamond measured for the first time on Mars at sol 13. The observed variation in the linewidth of the first-order 1332 cm^{-1} Raman line at room temperature of various types of diamond has been reported previously [6]. The diamond line width of a pure synthetic diamond, and type IIa diamond is found at ~ 1.68 – 1.87 cm^{-1}. Increase in linewidth of the 1332 cm^{-1} diamond line is found to be proportional to the concentration of the types of nitrogen impurities in the diamond lattice [6]. After correcting for the instrumental line width using Equation 1, the position and the linewidths of the diamonds sent to Mars measured with the micro-Raman system were found at 1332.1 $\pm$ 0.7 cm^{-1} with a linewidth of 4.2 cm^{-1} (Fig. 2). The type Ia diamonds selected for use as the SCCTs have a higher concentration of nitrogen impurity.

$$\omega_{\text{observed}}^2 = \omega_{\text{instrument}}^2 + \omega_{\text{intrinsic}}^2 \qquad (1)$$

The ω's in Eq. 1 refer to the *full width* at half-maximum of instrument resolution and intrinsic line width of the diamond, respectively.

The raw Raman spectra show that at various sols (e.g., sols 13, 238, 284, 341, 390, 424, 478 and 566), with ~ 3.6 mJ/pulse of the laser and ICCD gain of 2800, the diamond line is superimposed over a strong fluorescence background produced by the epoxy used to mount the diamond. The calculated spectrometer linewidth from the diamond line is in the range 12.1 and 12.4 cm^{-1}, close to the 12 cm^{-1} measured on the ground [2]. With a spectrometer FOV of 0.74 mrad, the instrument accepts light from the target at a distance of 1.58 m in the solid angle from the area of 1.06 mm^2, resulting in a relatively weak spectrum per pulse. In the case of diamond, 10 pulses are co-added on the ICCD chip and 10 co-added spectra are recorded to improve the signal to noise ratio (SNR). The data also require postprocessing to remove noise and spikes in the spectra [7]. This processing of spectroscopic data in the CDR (Calibrated Data Record) files result in the broadening of the Raman spectral lines of the targets.

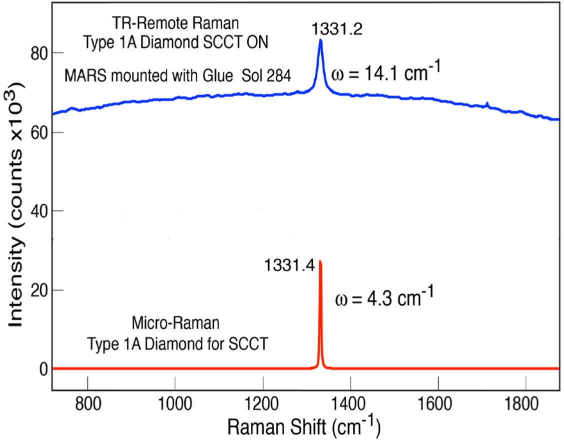

Figure 2. *Raman spectra of type Ia diamond plate (diameter 4 mm, 1 mm thick) selected for SuperCam Raman calibration targets: Bottom trace measured with micro-Raman spectrometer on the ground by O. Beyssac (personal communication), and the top trace measured at sol 284 on Mars with SuperCam's Transmission spectrograph.*

The second Raman SCCT selected for detecting organic-rich samples on Mars with the remote Raman technique is a polymer sample of a crystalline polyethylene terephthalate (PET, also known by its commercial name as Ertalyte). Between sols 12 and 627, the Raman spectra of Ertalyte was measured 12 times to evaluate the effect of UV radiation on organics on Mars. It has been found that the intensities of the characteristic Raman lines decrease relative to the fluorescence background due to UV radiation [8]. However, after 627 sols the characteristic line of the aromatic ring at 1615 cm^{-1} from Ertalyte is still observed [9]. To improve the SNR in the Raman spectra of various targets, higher laser power of the green beam ~7.18 mJ/pulse and ICCD gain of 3400 has been used for measuring the TR-Raman spectra. For example, on sol 410, Raman spectra of white paint on the rover were recorded with 20 accumulated pulses on the ICCD chip and 10 collected spectra in the computer. Table 1 shows the variation in wavenumbers of the Raman doublet for the CH stretch vibrations from the white paint along with the wavenumbers for the white paint peaks measured on the ground with the micro-Raman system in Spain.

TABLE 1. Raman line positions of the C-H doublet of rover white paint on Sol 410.

Shot No.	**ν_1 cm^{-1}**	**ν_2 cm^{-1}**	**$\Delta\nu$ (ν_1-ν_2) cm^{-1}**
1	2906	2974	67.8
2	2908	2964	55.2
3	2905	2963	57.5
4	2901	2966	64.8
5	2901	2963	61.7
6	2908	2963	54.4
7	2907	2964	57.5
8	2908	2967	58.8
9	2906	2964	58.2
10	2909	2965	56.8
Mean	2906.0	2965.3	59.3
Standard Dev.	2.7	3.4	4.3
Mean + St. Dev.	2908.7	2968.7	63.6
Micro-Raman White Paint sample on the ground			
	ν_1 cm^{-1}	**ν_2 cm^{-1}**	**$\Delta\nu$ (ν_1-ν_2) cm^{-1}**
Lorentzian	2907	2968	60.8

It is evident from Table 1 that there is an apparent shot-to-shot variation in the positions of the C-H stretching doublet. Similar effects were observed in the Raman spectra of most of the targets recorded with higher laser power. This variation may be due to low SNR or it may reflect the change in the wavelength of the laser oscillator operating at higher-laser power on Mars. Due to these effects, care must be taken in assigning peak positions of any organic molecule that may be detected. These results also highlight potential challenges in estimating the quantitative values of cation compositions in minerals such as the Mg-number from the Raman spectra of olivine observed in the Séítah formation in Jezero crater [10]. Overall, SuperCam has identified a number of minerals, including olivine, anhydrite, calcite, and Na-perchlorate, over the 640 Sols on Mars.

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