Introduction: The SuperCam instrument selected for the Mars 2020 rover is the integration of remote Laser-Induced Breakdown Spectroscopy (LIBS), Raman spectroscopy, time-resolved fluorescence (TRF) spectroscopy, visible and infrared (VISIR) reflectance spectroscopy, and a color remote micro-imager (RMI). Raman, TRF and VISIR are sensitive to the molecular structure of the sample from which one can definitively determine mineralogy and infer the elemental composition. LIBS is sensitive to the elemental composition from which geochemistry is definitively determined and mineralogy is inferred. This paper will focus on the Raman, TRF, and LIBS aspects of the SuperCam platform. The VISIR portion is discussed by [4].

Wiens et al. [1], Sharma et al. [2], and Clegg et al. [3] demonstrated that these complementary analytical techniques can be integrated into a single instrument suitable as a reconnaissance tool for other contact instruments as well as a primary science instrument. The SuperCam instrument is based on the ChemCam architecture that includes an infrared pulsed laser and telescope in the mast and a suite of three spectrometers in the body, connected by an optical fiber. On SuperCam the telescope on the mast will be used to focus a 1064 nm laser and generate a LIBS plasma from which the elemental composition will be determined up to a 7 m standoff distance. Some of the 1064 nm laser will be directed through a doubling crystal to produce 532 nm light for Raman mineralogical analysis to 12 m from the mast. The ChemCam visible and near infrared (VNIR) spectrometer will be replaced with a transmission spectrometer and intensified charged couple device (ICCD) that are designed to maximize the Raman mineralogical sensitivity. This transmission spectrometer and ICCD were also designed to collect time-resolved fluorescence spectra that can distinguish short lived organic fluorescence from long lived inorganic signatures. The SuperCam instrument also includes a VISIR reflectance spectrometer (400 – 900 nm, 1.3 – 2.6 µm) designed to remotely detect minerals [4]. Finally, the ChemCam black and white RMI that is integrated into the telescope will be replaced with a color RMI with the same spatial resolution to provide context images of the samples probed with the SuperCam spectrometers.

The Raman, TRF and LIBS techniques involve focusing a laser onto the surface of the sample, covering from several hundred microns to several millimeters enabling remote micro-scale geological investigations. Integration of these techniques into the same instrument ensures that the same sample locations are probed as the lasers are co-bore sighted. Finally, the SuperCam integrated instrument meets several important Mars 2020 mission goals including context mineralogy, fine scale imaging, fine scale elemental composition and organic detection, while the inclusion of a RMI similar to that on ChemCam satisfies the context imaging requirement [5].

Experimental: The data presented in this paper were collected with experimental hardware that simulates the SuperCam instrument performance. LIBS experiments involve the Los Alamos National Laboratory ChemCam testbed, a functional replica of the ChemCam instrument on Curiosity. ChemCam focuses a Nd:KGW laser (1067 nm, 3 Hz, 14 mJ/pulse) onto a sample surface. The laser ablates material from the surface, generating an expanding plasma containing electronically excited atoms, ions and small molecules. The excited species emit light at wavelengths diagnostic of the species present in the sample as they relax to lower electronic states. Some of this emission was collected with a 110 mm telescope and directed into the spectrometer suite.

The Raman experiments involve a separate experimental setup that directs a pulsed, doubled Nd:YAG laser (532 nm, 10 Hz, 10 mJ/pulse) onto the sample surface. The laser stimulates the Raman-active vibrational modes in the sample, producing the Raman emission. Some of this emission is collected with an 89 mm telescope and directed into the custom prototype miniature transmission spectrometer and recorded with an intensified charge couple device (ICCD) used to define the SuperCam transmission spectrometer. This transmission spectrometer was specifically designed to collect both the Raman signals to 4200 cm⁻¹ (685.1 nm) as well as record the LIBS signals out to 850 nm.

Samples: A broad suite of pure minerals were analyzed to 12 m by Raman and to 5 m by LIBS. The samples were placed in a vacuum chamber filled with 7 Torr CO₂ to simulate the Martian surface pressure.
The pure mineral samples included aragonite (CaCO$_3$), barite (BaSO$_4$), calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), gypsum (CaSO$_4$·2H$_2$O), jarosite (KFe$_{3+}$(SO$_4$)$_2$(OH)$_6$), olivine ((Mg,Fe)$_2$SiO$_4$), quartz (SiO$_2$), and talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$).

Discussion: Figure 1 contains Raman, LIBS, and TRF spectra from a gypsum sample that are representative of the data collected with a SuperCam-like platform of the minerals listed above. The LIBS spectrum is a characteristically simple CaSO$_4$ spectrum dominated by Ca emission lines. A hydrogen emission line at 656 nm is observed in the VNIR spectrometer indicating that the sample is either bassanite (CaSO$_4$·0.5H$_2$O) or gypsum (CaSO$_4$·2H$_2$O). The presence of potassium emission lines in the 770 nm region also suggests that the sample is not pure.

The Raman spectra of calcium sulfates produce many diagnostic peaks that can be exploited to differentiate anhydrite, bassanite and gypsum. The Raman spectra in Figure 1 are consistent with gypsum containing the 1008 cm$^{-1}$ SO$_4$ ion symmetric stretching modes.

Finally, the time resolved spectra in the bottom plot of Figure 1 also recorded broad fluorescence structures underneath the relatively sharp Raman features. The relative fluorescence intensity increases with opening the ICCD gate suggesting a relatively long fluorescence lifetime that is consistent with an inorganic impurity in the sample. In contrast, organic and biogenic samples tend to produce relatively short-lived fluorescence as described by Sharma et al. [6].

ChemCam and the Curiosity rover have encountered many occurrences of CaSO$_4$ in Gale Crater. Most of these observations appeared to be thin veins that ChemCam could probe independent of the surrounding host rock. ChemCam spectra are used to directly distinguish hydrated and dehydrated CaSO$_4$ based on the persistence of the H emission lines with sequential laser shots. ChemCam can also infer the presence of bassanite and gypsum from the extracted stoichiometry. The integration of the SuperCam Raman and VISIR spectrometers would definitively distinguish the observed CaSO$_4$ observations.

Finally, the sulfates described here define just one of many mineral classes that can be detected with the SuperCam instrument. SuperCam was also designed to detect the minerals listed above, phyllosilicate minerals, minerals in igneous rocks, the capabilities are set to observe relatively Raman-dark minerals, and many other minerals.

Conclusion: The SuperCam instrument suite is an integrated LIBS, Raman, time-resolved fluorescence, and visible and infrared reflectance spectrometer that has been selected for the mast of the Mars 2020 rover. SuperCam has the capability of remotely probing samples as both a reconnaissance tool as well as a primary science instrument capable of quantitative mineralogical and geochemical analyses.