

Combined Remote LIBS and Raman Spectroscopy of Minerals using a Single Laser Source. S. K. Sharma¹, A. K. Misra¹, P. G. Lucey¹, R. C. Wiens² and S. M. Clegg³, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd. HIG, Honolulu, HI 96822, USA (sksharma@soest.hawaii.edu), ²Space Science and Applications, Los Alamos National Laboratory, MS D466, Los Alamos, NM 87544, USA, ³Advanced Diagnostics and Instrumentation, Los Alamos National Laboratory, MS J565, Los Alamos, NM 87544, USA

Introduction: Raman spectroscopy (RS) and Laser-Induced Breakdown spectroscopy (LIBS) are highly complimentary techniques being developed to remotely probe the surface of geological samples. In general, LIBS uses a pulsed 1064-nm laser of high peak power ($>1 \text{ GW/cm}^2$) for ablating material from the surface of the sample to probe the elemental composition [1, 2]. Raman spectroscopy uses either a CW or a pulsed visible laser of modest average power (100-700 mW/cm²) to identify the molecular finger-prints of the sample from its Raman spectrum [3]. A combined remote Raman and LIBS system suitable for planetary science applications requires a single laser source with no moving parts. We have explored the use of a single pulsed laser operating at dual wavelengths of 1064 nm and 532 nm for exciting both the Raman and LIBS spectra of minerals by adjusting the laser power electronically.

Experimental Setup: Figure 1 is a diagram of the combined LIBS and Raman spectroscopy experimental setup. A detailed description of this combined system can be found elsewhere [4-6]. Both spectrometer systems probed samples placed in air or

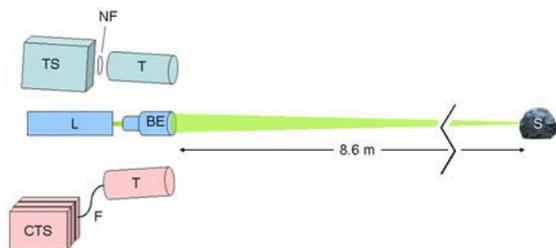


Fig. 1. Experimental set-up used for the LIBS and Raman spectra. TS = Raman transmission-grating spectrograph, NF = notch filter, T = telescope, L = laser, BE = beam expander, S = sample, F = fiber optic cable, CTS = Czerny-Turner spectrograph

in a vacuum chamber filled with 7 Torr CO₂ to simulate the surface pressure on Mars.

The combined Raman-LIBS system employed a Surelite Continuum Nd:YAG pulse laser (L) operating at 20 Hz, 7 ns pulse duration, and with a maximum pulse energy up to 130 mJ/pulse. Conversion of the 1064-nm laser beam into a second harmonic at 532-nm was adjusted so as to minimize the power at 532-nm (maximum power 25 mJ/pulse). A plot of total P_T (1064 nm + 532 nm) laser pulse energy and that of the 532 nm pulse (P_{532}) as a function of Q-switch delay time is shown in Fig. 2.

A 5x beam expander (BE) was used to focus both the 1064 and 532 nm laser beams onto the sample at 8.6 m from the beam expander (Fig. 1). Due to the chromatic aberration in the beam expander the 532-nm beam focused in front of the 1064-nm laser beam. Consequently, the diameters of the laser spot sizes on the sample located 8.6 m away were 600 μm and 900 μm for 1064 nm and 532 nm beams, respectively.

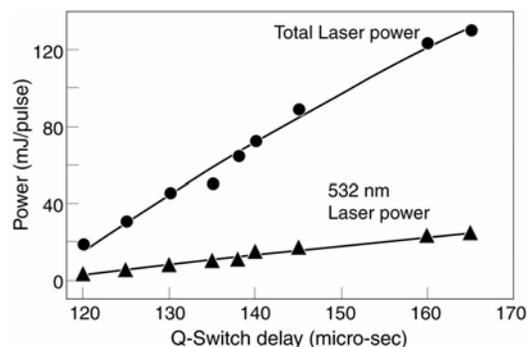


Fig. 2. Measured total laser pulse energy (P_T) of Nd:YAG laser simultaneously radiating both 1064 nm and 532 nm pulses, and of the 532 nm pulse energy ($P_{532\text{nm}}$) as a function of Q-switch delay. Q-switch delay was used to electronically control the laser power.

For the combined Raman and LIBS measurements, the signals excited by the Surelite Continuum laser were collected with a 125-mm-diameter reflecting telescope in oblique geometry, coupled directly to a Kaiser F/1.8 HoloSpec transmission-grating spectrograph (TS) through a 100- μm slit after passing through a 532-nm holographic super-notch filter (NF) to remove the reflected and Rayleigh-scattered laser light from the sample (Fig. 1). The detector was a Princeton Instruments intensified CCD detector. The HoloSpec spectrometer measured the Raman spectra from 70 cm^{-1} to 4500 cm^{-1} when excited with a 532-nm laser. The grating covered the spectral region from 534 to 699 nm, which was sufficient for identifying some of the major atomic emission lines of measured samples from their LIBS spectra. A 10.8-cm Newtonian reflecting telescope was used to collect some of this optical emission and direct the light into one of three Ocean Optics HR2000 spectrometers (CTS) through a 200- μm fused silica fiber (F) (Fig.1). The three spectrometers were similar to those that will be used for the ChemCam instrument, which includes the LIBS spectrometer selected for the Mars Science Laboratory (MSL) rover. These three spectrometers

record the emission in three regions: 225-320 nm ("UV unit"); 385-460 nm ("VIS unit"); and 500-930 nm ("NIR unit"). The positions of LIBS lines are estimated to be accurate within ± 0.02 nm.

The laser power of the Surelite Continuum Nd:YAG at the sample was electronically controlled by adjusting the Q-switch delay. As the laser pulse power was increased on the sample, we first observed the Raman spectrum of the sample excited by 532 nm beam followed by the LIBS spectrum when the 1064 laser power just reached the laser-breakdown point. At this breakdown point, both the Raman spectrum excited by a larger 532 nm beam and the LIBS spectrum excited within 600 μm diameter circle could be observed simultaneously. Further increase in the laser power created expanding plasma containing the electronically excited ions, atoms, and molecules from the surface of the sample. These electronically excited species emit light at frequencies indicative of the elements present.

Results: Figure 3 shows the combined Raman and LIBS spectra of calcite at 8.6 m in air in the 534-615 nm wavelength range.

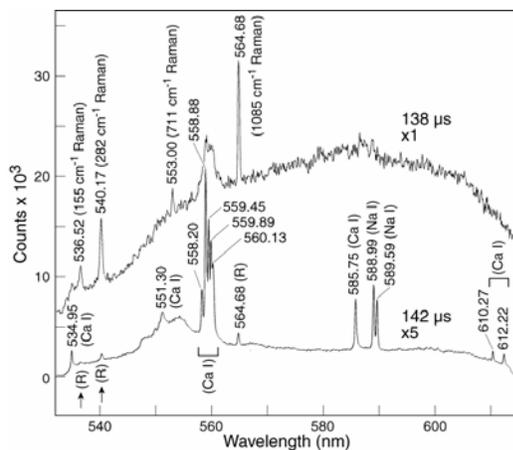


Fig. 3. Combined Raman and LIBS spectra of calcite at 8.6 min air in the 534-615 nm wavelength range. Band positions are marked in nm. Upper curve, the total laser pulse energy $P_T = 50.7$ mJ/pulse, and at 532 nm the pulse energy was $P_{532} = 9.3$ mJ/pulse. The P_T and P_{532} at Q-switch delay time of 142 μs were 77.3 mJ/pulse and 14.4 mJ/pulse, respectively.

At low power (138- μs delay), the upper spectrum in Fig. 3 shows Raman bands of calcites and broad fluorescence due to impurities in the sample. At high laser power (142 μs delay), in the bottom spectrum (Fig. 3) the LIBS signals are enhanced, Raman peaks are still detectable, and the fluorescence background is replaced by white continuum from the plasma. Along with calcium peaks, sodium is detected as the trace impurity element from its D_1 and D_2 lines at 588.99 and 589.59 nm.

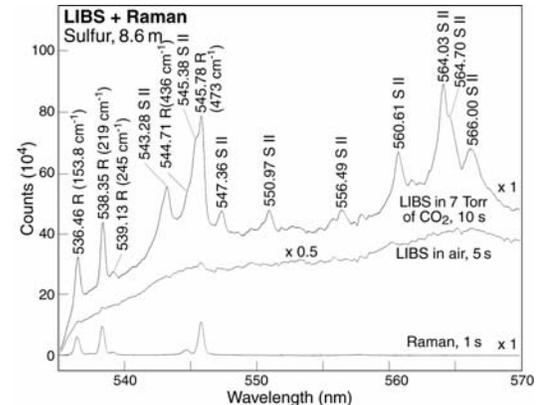


Fig. 4. Raman spectrum of sulfur from 8.6 m distance in air excited with 532 nm (5 mJ/pulse) (bottom spectrum). Middle spectrum, excited with total pulse energy $P_T = 50.3$ mJ/pulse and $P_{532} = 9.3$ mJ/pulse, shows no emission lines of sulfur species. Top spectrum measured in 7 Torr CO_2 shows both Raman and LIBS lines (Laser energy $P_T = 50.3$ mJ/pulse and $P_{532} = 9.3$ mJ/pulse).

Figure 4 shows the Raman and LIBS spectra of the solid sulfur both in air and in 7 Torr CO_2 . The Raman spectrum of sulfur excited with 5 mJ/pulse of 532 nm laser line in air is identified by the presence of strong Raman lines at 153.8, 219 and 473 cm^{-1} that are fingerprints of S_8 configuration in the solid [7]. Atomic S emissions are not observed in the LIBS spectrum in air even with P_T of 50.3 mJ/pulse and $P_{532\text{nm}}$ of 9.3 mJ/pulse at 8.6 m. The small bumps on the white continuum can be identified with the Raman lines (middle spectrum, Fig. 4). These experiments on the sulfur plate were also conducted in a vacuum chamber filled with 7 Torr CO_2 . The top spectrum in Fig. 4 recorded with integration time of 10 s shows combined LIBS and Raman lines. All of the LIBS lines at 545.38, 547.36, 550.97, 556.49, 560.61, 564.03, 564.70 and 566.00 nm could be identified as due to SII species [8, 9].

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