Long Range Remote Raman and LIBS Spectroscopy Using a Compact System with Low Laser Pulse Energy

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Introduction: Normally, large size remote Raman and LIBS systems are used for long range chemical detection over 100 m range. Using a 8 inch diameter telescope and a 100 mJ/pulse laser at 532 nm, we have successfully detected various chemicals from a distance of 430 m using Raman spectroscopy during daytime [1]. Similarly, the Univ. of Malaga holds the world record for conducting LIBS at the distance of 130 m using a large system utilizing a pulsed laser with 750 mJ/pulse at 1064 nm [2, 3]. Here, we describe a simple two component approach that helps to obtain remote Raman and LIBS spectra of targets at a distance of 246 m with 3 mJ/pulse in daytime and fast detection time of 1 s using a small remote Raman+LIBS system with 3 inch diameter collection optics [4]. This research work demonstrates a simple approach that significantly improves remote Raman and LIBS capabilities for long range chemical detection with compact low laser power Raman and LIBS systems.

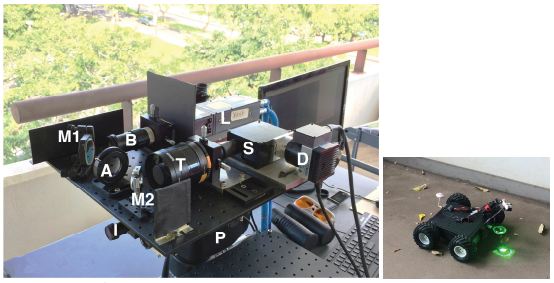

Fig. 1: (Left image) Compact remote Raman+LIBS system developed at the University of Hawaii using a 76 mm diameter telescope. L: Nd:YAG pulsed laser 532 nm, B: 8x beam expander, M1: laser mirror, A: aperture, M2: Mirror, T: telescope, S: compact Raman LIBS spectrograph, D: mini-ICCD detector, P: Pan and Tilt scanner, I: imaging camera. (Right image) Remote controlled car carrying a folding mirror and plano-convex lens for investigating distant chemicals on the ground.

System description and experimental details: The two component method consists of two parts, (i) a small remote Raman+LIBS system and (ii) a small remote lens near the target [4]. Figure 1(left image) shows a compact remote Raman+LIBS system developed at the University of Hawaii, which was used to acquire the data presented here. A small frequency-doubled Q-switched Nd:YAG pulsed laser source excites the distant targets. To acquire the data presented here the laser was operated at 3 mJ/pulse. An 8x beam expander is used to adjust the size of the laser spot to 50 mm in diameter at 246 m target distance. Two mirrors (M1 and M2) are used to align the laser beam with the optical axis of the telescope making it a coaxial system. The system uses a 500 mm, F8.0 mirror lens (Bower) as a telescope, which has a clear optical collection diameter of 68 mm and a central obstruction of 32.5 mm in diameter. The scattered light generated by the target is collected by the telescope and focused onto the 50 µm slit of a compact spectrograph of size 10 cm (length) x 8.2 cm (width) x 5.2 cm (height). The spectrograph covers the spectral range from 533 nm to 700 nm with pixel resolution of 0.06 nm and spectral resolution of 0.35 nm (FWHM) measured using a neon calibration lamp. The second component of the method is a small lens near the target, which could be carried by a field worker, a drone or a remote controlled car. Figure 1(right image) shows the mirror and lens assembly mounted on a remote controlled car to examine targets on the ground.

Samples: The liquid chemicals were ACS grade purchased from Fisher Scientific. The rock-forming mineral samples were from Wardôs Natural Science Establishment, Inc., Rochester, NY. The samples were measured without any preparation. Liquid samples were measured through 20 ml glass vials.

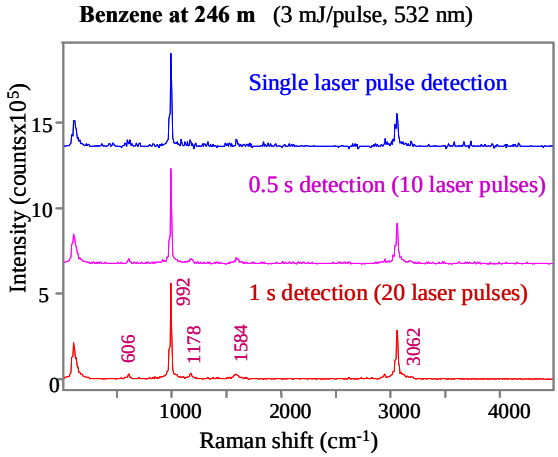

Fig. 2: Remote Raman detection of benzene from 246 m distance using 3 mJ/pulse, 532 nm and 2ò diameter focusing lens (f = 150 mm). Integration times: single pulse, 0.5 s, and 1 s.

Results and discussion: Figure 2 shows detection of benzene inside a 20 ml glass vial from 246 m distance with single pulse, 10 pulses and 20 pulses integration times and using low laser pulse energy of 3 mJ/pulse. A 2ò diameter lens with 150 mm focal length was used as the focusing lens near the target. Lens to target distance was 145 mm.

The ability to perform remote Raman spectroscopy from 246 m distance using low laser pulse energy is

a significant achievement in the field of remote chemical detection using fingerprint Raman signals. Raman signals are very weak and on average only one Raman photon is produced for every 10 million laser photons used for excitation. Despite the very low signal strength, a significant advantage of Raman spectroscopy is that it provides a very high level of confidence in chemical detection. Raman spectroscopy is capable of distinguishing between very similar chemicals. As an example, remote Raman spectra of benzene, ethyl-benzene and nitro-benzene from a distance of 246 m with 1 s integration time is given in Figure 3.

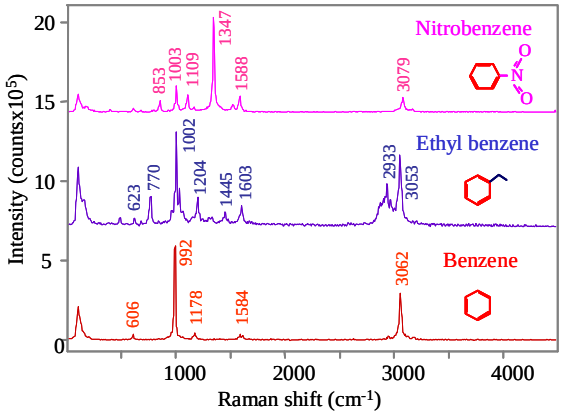

Fig. 3: Remote Raman detection of benzene, ethyl-benzene and nitro-benzene from 246 m distance with 1 s integration time using 3 mJ/pulse, 532 nm and 2ò diameter focusing lens (f = 150 mm).

The two component method was also used to test the remote LIBS capability. For the remote LIBS data, the position of the small lens near the target is adjusted so that it is exactly at the focal point.

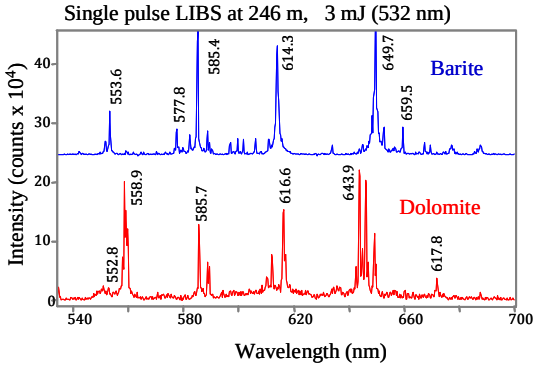

Fig. 4: Single pulse remote LIBS spectra of barite and dolomite mineral rocks from 246 m distance using 3 mJ/pulse of 532 nm pulsed laser and 2ò diameter focusing lens (f = 150 mm).

Figure 4 shows the remote LIBS spectra of barite ($BaSO_4$) and dolomite ($CaMg(CO_3)_2$) from a distance of 246 m using single laser pulse of energy 3 mJ. In the barite LIBS spectra all spectral lines correspond to Ba. In the dolomite spectra most of the atomic spectral lines correspond to Ca. Mg is observed at 552.84 nm and a Na doublet is observed at 589.0 and 589.59 nm. The ability to conduct remote LIBS from a target distance of 246 m with only 3 mJ/pulse is a new achievement. This is the longest target distance reported for performing LIBS.

Figure 5 shows the remote Raman spectra of barite and dolomite minerals. Both of these minerals were positively identified through their Raman fingerprint bands. In barite, symmetric stretching vibrations g_1 in the sulfate ions SO_4 is observed at 986 cm^{-1}. In the dolomite spectra the strongest peak at 1096 cm^{-1} corresponds to the symmetric stretching vibrational mode of the carbonate ion.

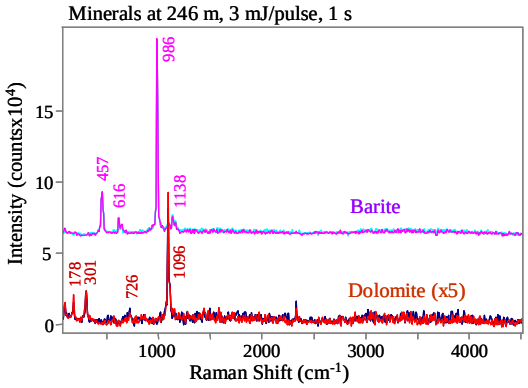

Fig.5: Remote Raman spectra of barite and dolomite minerals from 246 m distance with 3 mJ/pulse and 1 s integration time. Two measurements for both minerals are shown.

Summary: We describe a two component approach which significantly increases the remote Raman and LIBS capabilities using low laser power compact systems. The method is of especial interest to use of human in field operations on Earth and in the future NASA human missions to other planets where chemical analysis of field targets can be done by simply carrying simple optics without carrying the bulky instruments and without collecting samples. The data presented here suggest that simply attaching simple optics to the Mars Helicopter Scout in Mars2020 mission can also facilitate remote Raman and LIBS measurements of distant targets using the SuperCam instrument.

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References: [1] Acosta-Maeda T. E. et al. (2016) *Appl. Optics, 55*, 10283-10289. [2] Fortes F. J. and Laserna J. J. (2010) *Spectrochim. Acta, B 65*, 975-990. [3] Lopez-Moreno C. et al. (2006) *J. Anal. At. Spectrom., 21*, 55-60. [4] Misra A. K. et al. (2018) *Appl. Spectrosc*., https://doi.org/10.1177/0003702818812144.