

**A compact instrument for remote Raman and fluorescence measurements to a radial distance of 100 m** S. K. Sharma<sup>1</sup>, A. K. Misra<sup>1</sup>, P. G. Lucey<sup>1</sup> and C. P. McKay<sup>2</sup>, <sup>1</sup>Hawaii Inst. of Geophysics & Planetology, University of Hawaii, Honolulu, HI-96822, USA; ([sksharma@soest.hawaii.edu](mailto:sksharma@soest.hawaii.edu)), <sup>2</sup>NASA Ames, Space Science Division, Moffett Field, CA- 94035, USA.

**Overview:** Compact remote spectroscopic instruments that could provide detailed information about mineralogy, organic and biomaterials on a planetary surface over a relatively large area are desirable for NASA's planetary exploration program. Ability to explore a large area on the planetary surfaces as well as in impact craters from a fixed location of a rover or lander will enhance the probability of selecting target rocks of high scientific contents as well as desirable sites in search of organic compounds and biomarkers on Mars and other planetary bodies. We have developed a combined remote inelastic scattering (Raman) and laser-induced fluorescence emission (LIFE) compact instrument capable of providing accurate information about minerals, organic and biogenic materials to a radial distance of 100 m. Here we present the Raman and LIFE (R-LIFE) data set.

**Instrument:** Figure 1 shows the schematics of a prototype of a pulsed remote Raman system. The system consists of a 127-mm telescope (Meade ETX-125 Maksutov cassegrain, 1900 mm focal length), a frequency-doubled mini Nd:YAG pulsed laser source (model Ultra CFR, Big Sky Laser, 532 nm, 35 mJ/pulse, 20 Hz, pulse width 8 ns) [1,2]. The laser spot diameters at 100 and 10 m were 10 cm and 1 cm, respectively. A F/1.8 HoloSpec spectrometer was equipped with a small custom (2.5 cm high and 3.8 cm long) HoloPlex volume holographic phase grating, and a gated thermo-electrically cooled CCD detector.

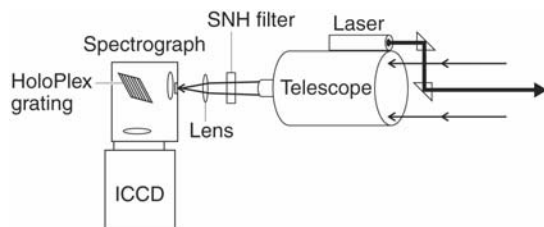


Fig. 1. Schematics of a directly coupled remote Raman set up

The CCD can be operated both in continuous wave (CW) and gated mode. The telescope is directly coupled to the spectrometer through a 20x (NA = 0.35, f = 20 mm) microscope lens. A 532 nm SuperNotch Plus holographic (SNH) filter is used in front of the microscope lens to minimize the unshifted reflected and Rayleigh scattered signal from the target.

**Results:** Figure 2 illustrates the use of HoloPlex grating to extend the Raman spectral range of the spectrograph in the 100-4400  $\text{cm}^{-1}$  range without degrading its spectral resolution. The Raman line frequencies of m-xylene are in agreement with literature values [3].

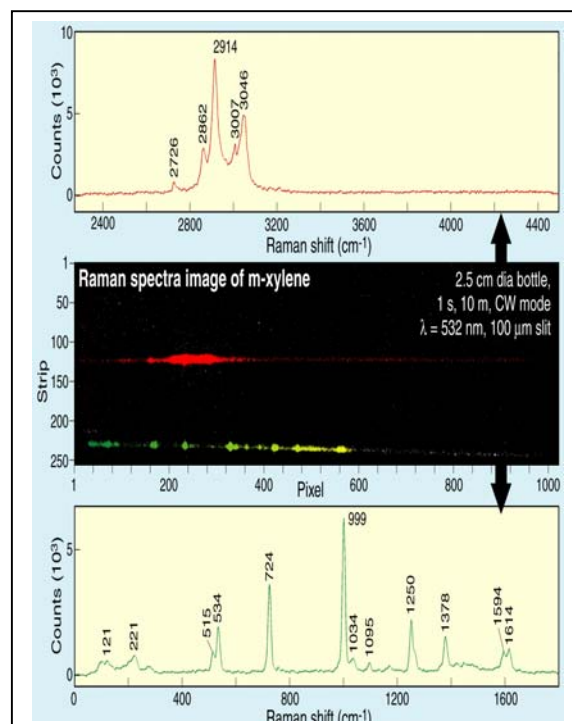


Fig. 2. Remote Raman spectral image of m-xylene at 10-m obtained with our prototype instrument in CW detection mode. The spectra is split into two parts and imaged on a common CCD detector. Laser 532 nm 20 Hz, 35 mJ/pulse, slit 100 micron, exposure time 1 sec (20 pulses).

Figure 3 shows the Raman spectra of calcite sample measured at distances of 100 m, 50 m, and 0.1 m with the above prototype instrument. All major Raman lines of calcite could be easily detected up to 100 m and are in agreement with previous literature within the experimental error of  $\pm 2 \text{ cm}^{-1}$  [4]. Capability of measuring spectra at various distances is an important feature of this prototype remote Raman system.

With this grating spectrometer, we have carried out Raman measurements on both solid, liquid and vapors of organic and molecular gases (naphthalene, benzene, cyclohexane, acetone,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , etc.), silicate,

and other oxy-anions containing minerals. Our R-LIF system enable us to detect the strongest spectral fingerprints of these materials [1-2]. In the remote Raman

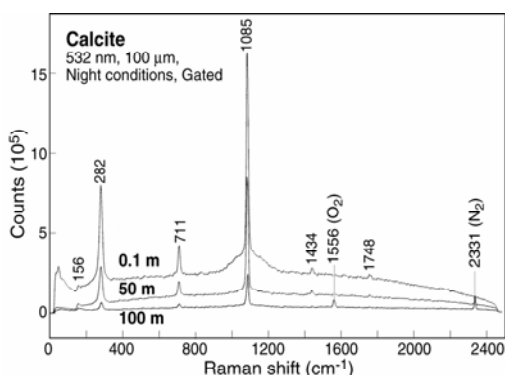


Fig. 3. Time-gated Raman spectra of calcite mineral at various distances. Laser 532 nm, 35mJ/pulse, 20 Hz, gate 1  $\mu$ sec, 200 laser shot accumulated (10 sec measurement time at 20 Hz). The Raman lines of atmospheric oxygen and nitrogen are clearly visible in the 100 m spectra.

spectra of compressed methane gas and solid CO<sub>2</sub> (dry ice) the characteristic doublet due to Fermi resonance of internal modes of vibration of CO<sub>2</sub> molecule were observed. In the Raman spectrum of CO<sub>2</sub> gas characteristic Fermi doublet appears at 1286 and 1388 cm<sup>-1</sup>. In the dry ice spectrum these sharp bands appear at 1278 and 1385 cm<sup>-1</sup>. The frequencies of CO<sub>2</sub> doublet in the remote Raman spectrum were within experimental error of  $\pm 1$  cm<sup>-1</sup> of the respective frequencies reported by Wang et al. [5]. In the Raman spectra of methane gas the symmetric stretching mode,  $\nu_1$  (A<sub>1</sub>) of CH<sub>4</sub> give rise to strongest Raman band. At 1 atm and room temperature the  $\nu_1$  mode of methane gas appears at 2916.5 cm<sup>-1</sup> [5], and its frequency is found to increase in solid CH<sub>4</sub> with increasing pressure. Because the Raman bands of CO<sub>2</sub> and CH<sub>4</sub> gases are sharp and well separated, it should be possible to detect concentrated plumes of methane gas in presence of carbon dioxide on Mars and other planetary surfaces with remote Raman spectroscopy.

Figure 4 shows the remote Raman and fluorescence spectra of green and yellow leaves of the Hawaiian Ti (*Cordyline terminalis*) plant and a piece of pinewood measured at a distance of 10 m in well-illuminated laboratory. It can be seen that the fluorescence signal from the green and yellow leaf samples are very strong compared to the Raman lines. The biological origin of the fluorescence is obvious with this gated measurement, where signals were measured with 1 micro second gate, indicating fast fluorescence lifetimes of the samples. The  $\nu_2$  (C-CH<sub>3</sub>),  $\nu_3$  (C-C) and  $\nu_1$  (C=C)

modes of vibration of carotene appear in resonance Raman spectra of red tomatoes<sup>20</sup> at 1004, 1155 and 1520 cm<sup>-1</sup>, respectively [6]. These resonance-Raman (RR) bands, characteristic of carotenes, have been observed in marine bacteria, fish eggs [7], and biogenic pink coral [8].

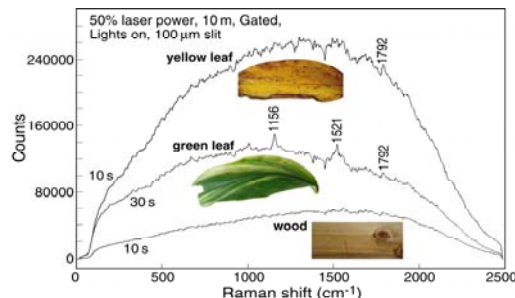


Fig. 4. Remote Raman and LIF spectra of (i) a piece of pinewood, (ii) a fresh Hawaiian Ti leaf (*Cordyline terminalis*) and a dead yellow Ti leaf. Laser power 17 mJ/pulse at 532 nm.

**Summary:** The data presented here show the ability of a combined remote Raman and LIF system to detect minerals, organics and various biogenic minerals and pigments to a radial distance of 100 meters. The instrument also has potential to contribute to Homeland Security and DOD applications requiring stand-off detection of chemical and biological agents.

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**References:** [1] Sharma S.K. et al. (2002) *Appl. Spectrosc.*, 56, 699-705. [2] Sharma, S.K. et al. (2003) *Spectrochim. Acta A*, 59, 2391-2407. [3] Sverdlov, L.M. et al. (1974) *Vibrational Spectra of Polyatomic Molecules*, John Wiley, NY. [4] White, W.B. (1985) in "Infrared and Raman Spectroscopy of Lunar and Terrestrial Materials" Ed., C. Karr, pp. 325-358. [5] Wang, A. et al. (2003) *J. Geophys. Res.* 108, E1, 5005-5023. [6] Haskins, C.L and Alexander, V. (1977) *Anal. Chem.* 49, 695-697. [7] Sharma, S.K. and Ayaka, T. (1997) in *Recent Advances in Marine Science and Technology '96*, pp. 227-237, PACON International, Honolulu, USA.. [8] Urmos, J.P. et al. (1991) *Amer. Mineral.*, 76, 641-646.