

**SINGLE PULSE REMOTE RAMAN DETECTION OF MINERALS AND ORGANICS UNDER ILLUMINATED CONDITION FROM 10 METERS DISTANCE.** A. K. Misra, S. K. Sharma, P. G. Lucey; Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, 2525 Correa Rd. HIGP, Honolulu, HI 96822, USA; ([anupam@hawaii.edu](mailto:anupam@hawaii.edu))

**Overview:** A directly coupled portable remote Raman instrument developed by the University of Hawaii has been shown here to identify several minerals, chemicals and organics from a distance of 10 m using a single laser pulse in a well illuminated background. Raman spectra, obtained during a very short period of time, of common minerals e.g., dolomite, calcite, marble, barite, gypsum, quartz, rutile, fluorapatite etc. clearly show Raman features which could be used as fingerprints for mineral identification. Raman features of organics such as benzene, cyclohexane, 2-propanol, naphthalene, etc. and other chemicals containing various functional groups like oxides, silicates, sulphates, nitrates, phosphates and carbonates were also easily detected. Ability to measure Raman spectra with a single laser pulse would be promising for future space missions where power consumption is critical and a rapid survey of the minerals with moderate to high Raman cross section might be desirable for selecting rocks that would provide high scientific return or for acquiring rocks for sample return to the Earth.

**Introduction:** Raman Spectrometers traditionally thought of limited to measuring signals in the dark labs using bulkier system is no longer the trend. With the development of efficient CCD and spectrographs, Raman systems are becoming compact and popular in analytical laboratories. Integrating these small spectrographs with compact lasers has made it possible for developing portable Raman systems. Such a portable remote Raman system has been developed at the University of Hawaii and successfully tested to obtained Raman spectra of minerals and organics from distances over 10 to 50 m in daylight condition [1,2]. In order to measure Raman spectra in daylight or under well illuminated background, it is important to use a pulse laser source and a gated detector [1,2]. Such a combination significantly improves the signal to background ratio of Raman peaks which are known to have very weak cross-sections in comparison to Rayleigh or Mie scattering cross-section. Gated system also helps in reducing long-lived fluorescent background generated by inorganic fluorescent impurities, e.g., transition ions and rare-earth ions [3-5].

**Experimental Set-up and Samples:** The pulsed remote Raman system has been described in detail elsewhere [1,2,6]. In brief it consists of a 127-mm tele-

scope (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, central laser spot divergence 0.8 mrad), a Kaiser F/1.8 Holospec spectrometer equipped with a gated thermo-electrically cooled CCD detector. The telescope is directly coupled to the spectrometer through a 20x (NA = 0.35, long focal length = 20 mm) microscope lens. A 532 nm SuperNotch Plus holographic filter is used in front of the microscope lens to minimize the Rayleigh scattering signal from the target. Single pulse Raman spectra were measured in an oblique mode where the laser is directly aimed at the distant target (placed at 10 m) and the telescope collects the scattered radiation at an oblique angle of 1 degree. All spectra were measured using a 100 micron slit with the intensified CCD in the gated mode in the lab with all lights turned on. The integration time for each of the spectra was 0.05 seconds (equivalent time for a single pulse from the 20 Hz laser). Actual Raman signals were collected in 1.1 micro-second duration corresponding to gate width of the detector. No cosmic ray or baseline corrections were applied to spectra presented here. A 10 point binomial smoothing (using GRAMS/32<sup>®</sup> software package) was used in the presented spectra. Neon lines were used in calibrating the spectra and measured single pulse Raman spectra of benzene and cyclohexane verified peak positions within  $\pm 2 \text{ cm}^{-1}$  of standard values obtained from the NIST website.

The rock-forming mineral samples were purchased from Ward's Natural Science Establishment, Inc.,

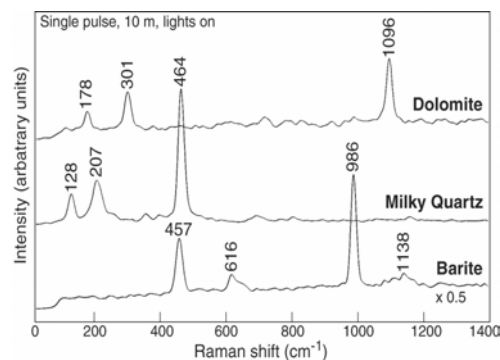


Figure 1: Raman spectra of dolomite, milky quartz, and barite using a single 532 nm laser pulse from a distance of 10 m with all lab lights on.

Rochester, New York. These samples were used without any polishing or cutting. The dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) sample was from Bamble, Norway, milky quartz ( $\text{SiO}_2$ ) was from Dekalb, New York, and barite ( $\text{BaSO}_4$ ) was from Potosi, Missouri. Rutile ( $\text{TiO}_2$ ), sodium phosphate monobasic dehydrate ( $\text{NaH}_2(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ), and barium nitrate,  $\text{Ba}(\text{NO}_3)_2$  were analytical grade chemicals in the powder form obtained from Fisher Scientific, USA.

**Results:** Figure 1 shows single pulse remote Raman spectra from 70 to  $1400 \text{ cm}^{-1}$  range of dolomite, milky quartz and barite. The symmetrical stretching modes of oxygens of carbonate ions ( $\nu_1$  ( $\text{CO}_3$ )) in dolomite, of  $\alpha$ -quartz ( $\nu_s$  (Si-O-Si)) and of sulphate ( $\nu_{1g}$  ( $\text{SO}_4$ )) in barite, respectively at  $1096 \text{ cm}^{-1}$ , at  $464 \text{ cm}^{-1}$ ,  $986 \text{ cm}^{-1}$  are clearly distinguishable (Fig.1). The positions

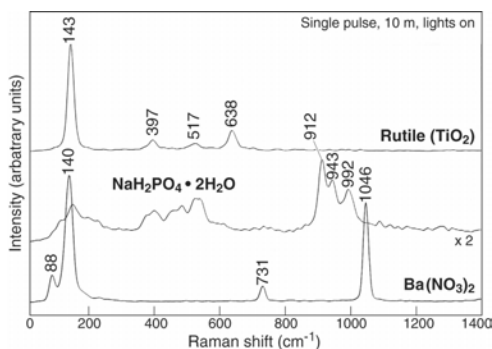


Figure 2: Remote Raman spectra of rutile, sodium phosphate monobasic, dihydrate and barium nitrate from 10 m using single laser pulse.

of these Raman lines are within  $\pm 2 \text{ cm}^{-1}$  of the values reported in the literature [7-9].

Figure 2 shows the Raman spectra of rutile ( $\text{TiO}_2$ ), sodium phosphate monobasic, dihydrate ( $\text{NaH}_2(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ) and barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ . Once again, Raman spectra for each chemical show unique spectral patterns, and hence are suitable for identifying the various functional groups such as sulphates, nitrates, carbonates, silicates, and phosphates. It is also possible to distinguish various minerals within the same functional group, e.g., calcite, magnesite, dolomite from each other using the positions of the low-frequency lattice modes and mid-frequency internal modes [10-11].

Work presented here clearly demonstrates that it is possible to measure Raman spectra with clear features of various organics, chemicals and minerals using only a single laser pulse with our portable remote Raman system. Significant improvement in the quality of the spectra is expected when spectra is accumulated over several pulses. This is shown in figure 3 which compares the Raman spectra of barite, at 10 m distance,

using 75% of laser power (26 mJ/pulse), with 1 pulse ( $t = 0.05\text{s}$ ), 10 pulses ( $t = 0.5\text{s}$ ) and 20 pulses ( $t = 1 \text{ s}$ ). No binomial smoothing was applied to these spectra. With the improvement in the signal to noise ratio, the weaker Raman bands could be easily detected.

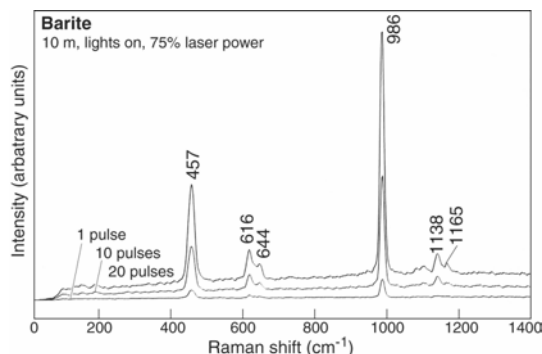


Figure 3: Comparison of Raman spectra of barite using single pulse, 10 pulses and 20 pulses (Laser 532 nm, 20 Hz, 26mJ/pulse, target at 10 m, detector gated, 100 micron slit, lights on.)

**Summary :** The data presented here show the ability of a portable remote Raman system to detect minerals, organics and various inorganic chemicals from a distance of 10 meters in well illuminated background. Such system would be ideal for identifying minerals on a planetary surface in daylight condition [2,7].

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