

**Compact Portable Remote Raman System for Planetary Exploration and Rapid Detection of Water and Hydrous Minerals.** S. K. Sharma, A. K. Misra, T. Acosta, D. Bates and P. G. Lucey, Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, Honolulu, HI 96822, USA; [sksharma@soest.hawaii.edu](mailto:sksharma@soest.hawaii.edu)

**Overview:** Exploration of minerals and search for water, carbon and evidence of biomarker has become an important part of NASA's planetary missions in order to search for life on other planets. Water has been detected on Mars in the form of ice and in hydrous minerals. Among the various techniques for detecting water, ice, and H<sub>2</sub>O/OH bearing minerals, Raman spectroscopy stands out as providing distinctive spectra for unambiguous identification of water and water bearing minerals.

University of Hawaii has been developing small portable remote Raman system for planetary explorations. Portable remote Raman instrument previously developed at the University of Hawaii utilizing 5 inch telescope has been shown earlier to detect water, ice, and water bearing minerals, carbon in carbonate form in calcite, magnesite, dolomite, siderite etc. from a distance of 10 to 50 m under bright day conditions with short integration time [1-3]. Recently, we have significantly reduce the size of our remote Raman system in order to develop miniature Remote Raman system suitable for future space missions. It is shown here that good quality Raman spectra of various minerals, water, water-ice, CO<sub>2</sub>-ice, organic and inorganic chemicals etc. could be easily obtained from remote distances with a compact remote Raman system utilizing only a regular 85 mm Nikon camera lens as collection optics replacing the 5 inch telescope and with 1 s of integration time. The remote Raman system also uses a small Raman spectrograph developed at the University of Hawaii which is 1/14<sup>th</sup> in volume in comparison to commercial spectrograph from Kaiser Optical System Inc. used in the previous work [1-3].

The compact Remote Raman system would be attractive analytical probe for the future Mars and Venus mission, where rapid analysis of the landscape could be easily performed. The ability to detect water and other minerals from remote distances during daytime would be also promising for analyzing targets at hard to reach places such as lakes, cliffs, craters, etc.

**Experimental Set-up and Samples:** The schematics of pulsed remote Raman system has been described in detail elsewhere [1-4]. In the present work we have replaced the telescope with a 85 mm Nikon camera lens. A two inch diameter 532 nm notch filter is used in front of the camera lens to block off the Rayleigh scattered light. 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 of 7 mm at 9 m) is used in an oblique geometry to excite the target located at a remote distance. The scattered light generated by the target is collected by the Nikon camera lens which then focusses it onto the slit of the compact spectrograph of size 10 cm (length) x 8.2 cm (width) x 5.2 cm (high). The spectrograph was constructed using a custom HoloPlex grating from Kaiser Optical System Inc. (Spectral Coverage +100 cm<sup>-1</sup> to 4445 cm<sup>-1</sup>; Stokes-Raman shifted from 532 nm laser excitation). The spectrograph is equipped with a gated thermo-electrically cooled ICCD detector. Figure 1 shows the photograph of the compact remote Raman system.

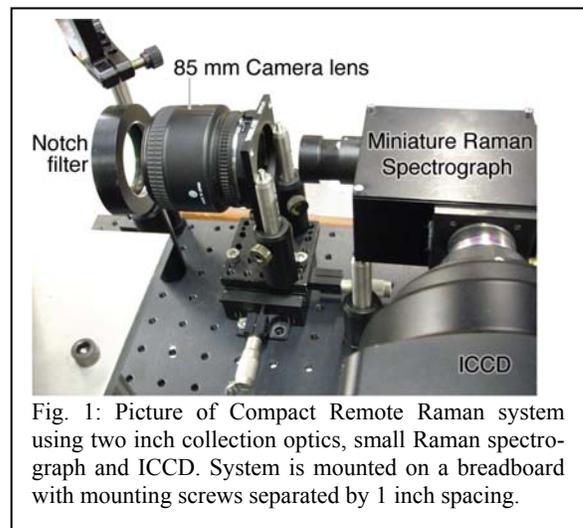


Fig. 1: Picture of Compact Remote Raman system using two inch collection optics, small Raman spectrograph and ICCD. System is mounted on a breadboard with mounting screws separated by 1 inch spacing.

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. Samples were placed 9 m away from the Nikon camera lens. Spectra were measured with integration time of 1s in gated mode with gate width of 4  $\mu$ s. No cosmic ray or baseline corrections were applied to the spectra presented here.

Neon lines were used in calibrating the spectra and measured Raman spectra of benzene and cyclohexane verified peak positions within  $\pm 2$  cm<sup>-1</sup> of standard values obtained from the NIST website [5].

The rock-forming mineral samples (gypsum, anhydrite, barite, dolomite, quartz, spodumene etc.) were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. These samples were used without any polishing or cutting. Water bearing compounds were analytical grade chemicals in the powder/bulk form from Fisher Scientific, USA. Water sample was drinking tap water.

**Results:** Figure 2 shows the entire Raman spectra of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Gypsum),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in frequency region, 100 to  $4445 \text{ cm}^{-1}$ ,

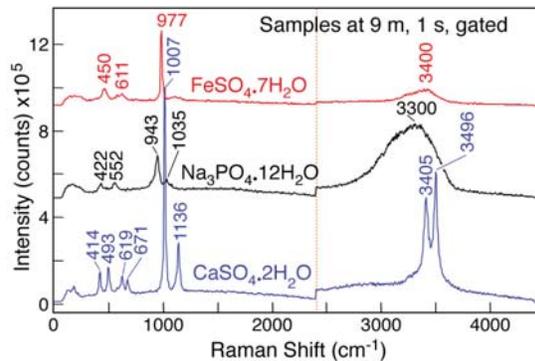


Fig. 2: Remote Raman spectra of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Gypsum),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in frequency region, 100 to  $4445 \text{ cm}^{-1}$ , from a distance of 9 m with integration time of 1 s. Laser 532 nm, 35 mJ/pulse, 20 Hz. Raman peaks near  $3300\text{--}3500 \text{ cm}^{-1}$  region are due to water molecules.

from a distance of 9 m with integration time of 1 s. The fingerprint Raman bands of these minerals are marked on the plot. The symmetrical stretching mode of sulfate ions ( $\nu_1(\text{SO}_4^{2-})$ ) in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is observed at  $1007$  and  $977 \text{ cm}^{-1}$ , respectively. The strong peak at  $943 \text{ cm}^{-1}$  in the  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  spectrum corresponds to symmetrical stretching modes of phosphate ions ( $\nu_1(\text{PO}_4^{3-})$ ). Very strong bands near  $3300\text{--}3500 \text{ cm}^{-1}$  in Raman spectra of hydrous minerals indicate the stretching modes of a chemically bonded water molecule. The chemically bonded water molecules in gypsum are observed at

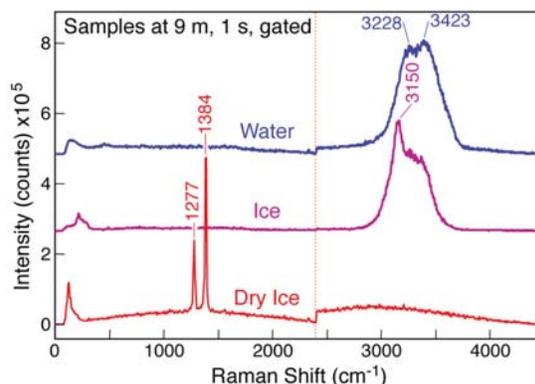


Figure 3: Remote Raman spectra of water, ice and dry ice (solid  $\text{CO}_2$ ) from 9 m with 1s integration showing distinct water and  $\text{CO}_2$  Raman bands.

$3405 \text{ cm}^{-1}$  and  $3496 \text{ cm}^{-1}$ . Because of the chemical bonding of water with the minerals, water molecules can exist in these minerals at temperatures significantly above the boiling point of liquid water under reduced pressure of 7 torr of  $\text{CO}_2$  on Mars.

Figure 3 shows the remote Raman spectra of water, ice, and  $\text{CO}_2$  ice (dry ice) from a distance of 9 m and 1 s integration time. Water gives very strong Raman signal in the  $3100\text{--}3600 \text{ cm}^{-1}$  spectral region, and it is easy to detect water in various forms even with a single laser pulse excitation. In the liquid water sample, strong broad Raman bands near  $3228$  and  $3423 \text{ cm}^{-1}$  are the symmetric ( $\nu_1$ ) and antisymmetric stretching ( $\nu_3$ ) vibrational modes of the water molecule, respectively. Ice can be distinguished from liquid water by the presence of a sharper band at  $3150 \text{ cm}^{-1}$ . The sharpening of the H-O-H symmetric stretching mode of water indicates increasing ordering in the water ice structure and the shifting of the band towards lower frequency is caused by strengthening of hydrogen bonds in the ice.

In Raman spectrum of  $\text{CO}_2$  gas, the  $\nu_1$  totally symmetric stretching vibration of  $\text{CO}_2$  ( $1305.4 \text{ cm}^{-1}$ ) is active for the isolated molecule and is in Fermi resonance with the  $2\nu_2$  overtone of the i. r. active bending mode of the molecule ( $\nu_2 \sim 667 \text{ cm}^{-1}$ ). As a consequence, two intense peaks are observed giving rise to the so-called Fermi doublet. The spectrum of dry ice also shows two strong  $\text{CO}_2$  Raman lines of Fermi resonance doublet at  $1277$  ( $2\nu_2$ ) and  $1384$  ( $\nu_1$ )  $\text{cm}^{-1}$  [6].

**Summary:** The data presented show the ability of a portable compact remote Raman system to detect water, ice and water bearing minerals from a distance of 9 meters in a well illuminated background with 1 s integration time. Such system would be ideal for identifying minerals and searching for water on a planetary surface during daylight and nighttime.

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**References:** [1] Sharma, S. K., et al. (2002) *Appl. Spectrosc.*, **56**, 699-705. [2] Misra, A. K., et al. (2005) *Spectrochim. Acta, A* **61**, 2281. [3] Misra, A. K., et al. (2006) *Appl. Spectrosc.*, **60**, 223-228. [4] Sharma, S. K., et al. (2003) *Spectrochim. Acta A*, **59**, 2391-2407. [5] NIST Standard Reference Database Website: <http://webbook.nist.gov/chemistry/>. [6] Sharma, S. K. et al. (2004) *LPSC*, **35**, #1929.