

REMOTE PULSED-LASER RAMAN SPECTROSCOPY SYSTEM FOR MINERAL ANALYSIS. Shiv. K. Sharma¹, S. Michael Angel², Manash Ghosh¹, Hugh W. Hubble¹ and Paul G. Lucey¹, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI 96822. (sksharma@soest.hawaii.edu), ²University of South Carolina, Dept. of Chemistry & Biochemistry, Columbia, SC29208.

Introduction: There is a need for an instrument that can be used for remote *in situ* identification of biogenic and a-biogenic minerals, various types of ices, organic materials etc. on planetary surfaces. The potential for measuring remote-Raman spectra of organic [1] and inorganic materials and minerals [2] with a small telescope and CW lasers have been demonstrated. Pulsed-laser Raman spectroscopy, or simply pulsed-Raman spectroscopy, is a very powerful technique for identifying both inorganic and organic materials from their unique vibrational signatures. Pulsed Raman techniques offer two important benefits: namely, (i) discrimination against unwanted ambient light, and (ii) discrimination against long lived fluorescence emission from the sample [3]. With pulsed Raman techniques high quality Raman spectra of minerals and melts at high temperatures have been measured for investigating phase transitions and anharmonicity of various vibrational modes [4].

Advancements in solid-state lasers and gated ICCD detectors have made it possible to develop a compact and lightweight Raman system for remote analysis of mineral surfaces. In this paper, we present results of our pulsed-Raman measurements at a distance of 10's of meters in the laboratory as well as in an outdoor environment.

Experimental: The remote pulsed-Raman system consists of a 5-inch telescope, a 20 Hz frequency doubled Nd:YAG laser source and a ¼ meter spectrometer and gated intensified detector. Samples were placed at a distance of 10 to 66 meters from the telescope and were excited with a 532-nm laser pulse, with ≤ 35 mJ/pulse, from the frequency doubled Nd:YAG laser (Model ULTRA CFR, Big Sky Laser). The width of the laser pulses was 8 nanosec (ns), and the beam divergence was <8 mrad.

The scattered light from the sample was collected using the telescope (Meade ETX-125). This Maksutov-Cassegrain telescope has a 127-mm clear aperture and a focal length of 1900 mm. The ULTRA CFR laser head was mounted along the length of the telescope tube. The laser beam was made coaxial with the telescope axis using two small dichroic mirrors.

Raman spectra were recorded with a Spex 0.25 meter imaging spectrograph (Model 270M) equipped

with a ruled grating of 1800 grooves/mm blazed at 500 nm, and with a thermoelectrically cooled (-20° C), gated and intensified ICCD detector (Model I-Max ICCD Princeton Instruments, Inc.). We used an optical fiber of 1-meter length and 200- μ m diameter to couple the telescope output with the spectrometer. The output of the telescope was collimated with a lens. A holographic super-notch filter was inserted between the collimating lens and a 10X microscopic objective that focussed the light at the end of the fiber. The super-notch filter was adjusted to attenuate the elastically (Rayleigh and Mie) scattered and diffuse reflected light.

We used benzene as a test sample to measure the performance of this system. We recorded an excellent Raman spectra of benzene with high signal to noise ratio to a distance of ~ 66 meters using as few as a single laser pulse. Measuring the remote-Raman spectra of a marble (CaCO_3) and silicate and hydrous minerals further verified the system performance.

Results and Discussion: Figure 1 shows the fingerprint region of the Raman spectra of benzene recorded with the pulsed-Raman system in an out

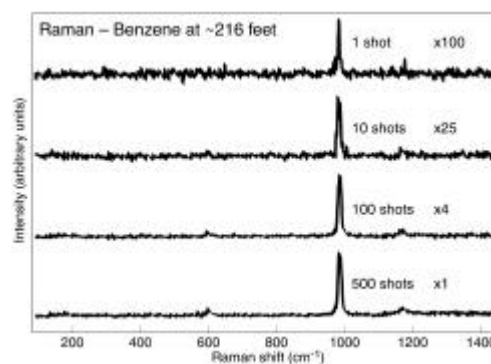


Fig. 1. A part of remote pulsed-Raman spectra of benzene at a distance of ~ 65 meters.

door location with various integration times (number of laser shots), with a slit width of 400 micrometers. We were able to detect the strong A_{1g} Raman line of benzene [5] at 991 cm^{-1} with a single laser shot of 35mJ/pulse with detector being active for 15-ns. By integrating the spectra over 10, 100, and 500 shots - corresponding to the times of 0.5, 5 and 25 sec for the 20 Hz laser, respectively - significant improvement in signal to noise ratio was achieved (Fig. 1).

Since the gate of the ICCD detector can be open for as short period as 15 ns, interference from background radiation is effectively suppressed. In the spectra recorded with 100 and 500 shots, weak benzene bands corresponding to two E_g^+ modes near 607 and 1178 cm^{-1} are clearly visible [5].

Portions of remote-Raman spectra of a marble sample, in the 100–1400 cm^{-1} recorded in the laboratory at a distance of ~ 10 meters using 200 micrometers slit widths and the 532 nm laser excitation with 35 mJ/pulse are shown in Fig. 2. In a single-shot spectrum the low frequency lattice modes at 154 and 281 cm^{-1} are clearly visible along with a strong internal mode of carbonate at 1085 cm^{-1} . As expected, the signal to noise ratio in the spectra of marble improves with integration of the data over more laser shots (Fig. 2). In the spectrum with two laser shots of 35 mJ/pulse, the weak band at 711 cm^{-1}

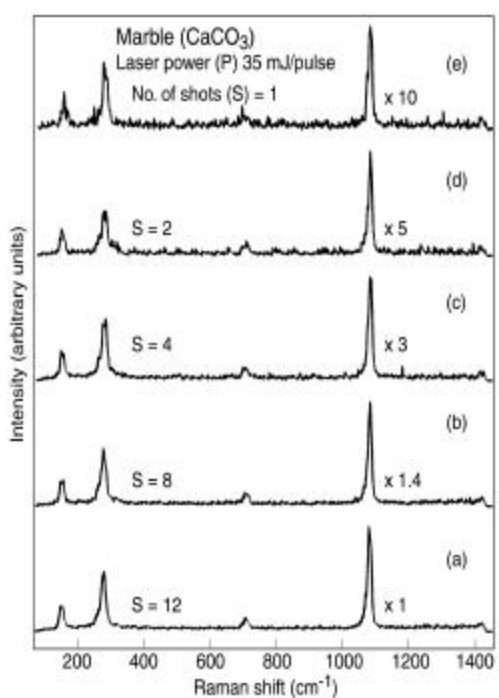


Fig. 2. Parts of remote Raman spectra of marble at a distance of ~ 10 meters.

is clearly visible. These Raman bands in the spectrum of marble are characteristic of CaCO_3 crystallized in the calcite structure [6]. Measurements of the remote-Raman spectra as a function of laser power indicated that good quality spectra of marble are obtained with 17.5 mJ/pulse and by suitably binning the ICCD chip.

Raman spectra of dolomite ($\text{CaMg}(\text{CO}_3)_2$) recorded as a function of distance are shown in Fig. 3. With 500 laser shots and by binning the ICCD over

3-pixel along the wave number axis, the spectra of dolomite in the 100–1400 cm^{-1} region with good signal to noise were recorded (Fig. 3). The low frequency lattice modes at 175 and 299 cm^{-1} are char-

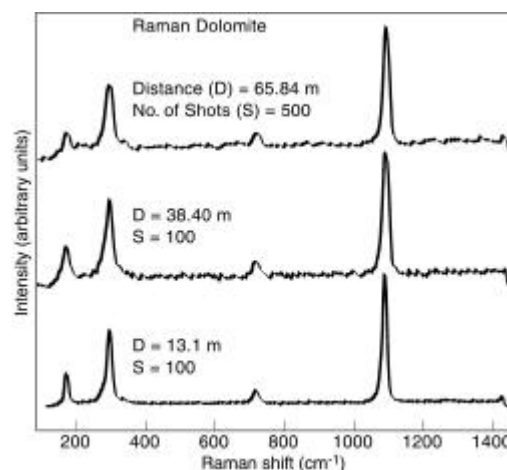


Fig. 3. Parts of pulsed-Raman spectra of dolomite recorded at various distances out doors. The spectra at 13.1, 38.4 and 65.84 meters were recorded by binning the ICCD along the wavenumber axis with 1, 2 and 3-pixels, respectively.

acteristic modes of the dolomite lattice. The band at 724 and 1097 cm^{-1} are internal modes of carbonate ions in dolomite [6]. We have also measured good quality Raman spectra of silicate, and hydrous silicate and sulfate minerals, indicating that the remote-pulsed Raman system can be used to analyze the mineral on planetary surfaces to a distance of 10 to 66 meters.

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