

RAMAN SPECTROSCOPY SYSTEM FOR MINERAL ANALYSIS ON PLANETARY SURFACES

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ABSTRACT

There is currently a need for a lander-based or rover-based instrument to characterize minerals on planetary surfaces due to future missions planned to the moon and Mars. Several papers have proposed a Raman spectroscopy system for such instrument because of many advantages of its many advantages over other techniques. In this paper, three Raman spectroscopy systems developed by three different research groups are discussed.

INTRODUCTION

As proposed by several papers, Raman spectroscopy is the best suited tool for analyzing minerals on planetary surfaces.¹⁻⁵ Raman spectrum of minerals and their mixture yields sharp non-overlapping spectral features, resulting in much less ambiguous detection. Other spectroscopy techniques suffer from broad overlapping features that complicate the interpretation of their spectra.¹⁻⁵

Presently, a handful of research groups around the country are developing Raman spectroscopy systems that are specifically designed to be compact and able to be integrated with robotic rovers or landers to analyze minerals on planetary surfaces.¹⁻⁵

Wang, et al. developed the Mars microbeam Raman spectrometer, which is designed for close-up analysis of rocks and soils in planetary surface exploration.¹ Close up analysis is made possible by a probe contained in a flight unit to be deployed and operated by a robotic arm. This system not only identifies major, minor, and trace minerals; it can also obtain approximate relative proportions of such minerals, and determine chemical features and rock textural features.

Sharma, et al. developed the remote Raman spectroscopy system. This remote system is designed to perform Raman analysis remotely from distances in the order of tens of meters. This system utilizes a pulsed laser for excitation of remote sample, and a telescope for collecting the scattered signal.²

At NASA Langley Research Center, a Raman spectroscopy system similar to the one by Sharma, et al. is also being developed.⁵ This system is also designed to remotely obtain Raman spectrum of organics and minerals on planetary surfaces. It also utilizes a pulsed laser and a telescope to enable remote measurement.

In the proceeding sections, each of the three systems mentioned is discussed in detail.

RAMAN SPECTROSCOPY SYSTEMS

Mars Microbeam Raman Spectrometer

The Mars microbeam Raman spectrometer (MMRS) was developed by Wang, et al. at Washington University in St. Louis, Missouri. The MMRS is designed for close up analysis of rocks and soils in planetary surface. A schematic diagram of the MMRS is shown in figure 1.¹

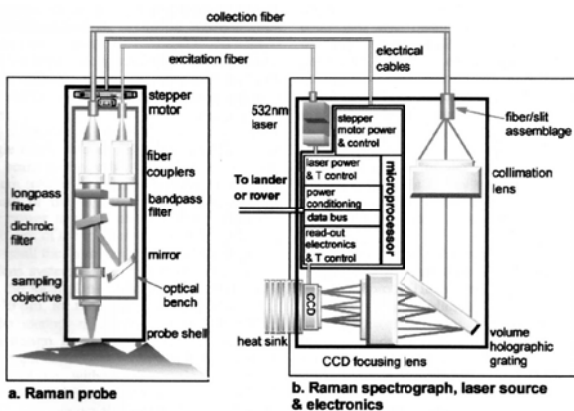


Figure 1. Schematic diagram of the MMRS showing the probe and the main body, and the various electrical and optical components inside (From Ref. 1).

The MMRS has a probe that will be deployed and operated by a robotic arm. This probe allows close-up analysis of surfaces by bringing the laser signal and the backscattering collection optics close to the sample.

The main body of the MMRS will be housed inside the vehicle. The main body will contain the laser, the spectrograph, and the CCD. Two fiber optic cables (collection fiber and excitation fiber) and one electrical cable connect the probe and the main body.

An example of data taken with the MMRS is shown in figure 2, which shows the spectra of calcite, olivine, quartz, feldspar, and pyroxene.¹ The spectra required varying integration times to

obtain the characteristic peaks of each sample. This data was compared to a commercially produced laboratory Raman system, and the MMRS exhibited comparable results.

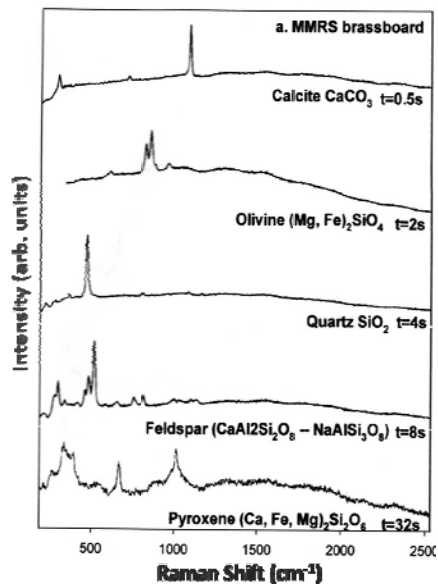


Figure 2. Spectrum of some minerals taken by the MMRS (From Ref. 1).

The MMRS demonstrates that a suitably miniaturized, sufficiently robust, and low power usage Raman spectrometer can be built to serve as an on-surface planetary instrument. Furthermore, the MMRS can retain high detection sensitivity and yield near laboratory quality spectra over a broad wavelength range.

Remote Raman Spectroscopy System

Sharma, et al. from University of Hawaii developed the remote Raman spectroscopy system. This small portable system was developed for standoff distance of the order of several meters.²⁻⁴ It is designed to collect the Raman spectra in high-background condition such as outdoors during daytime or in a well-illuminated lab. A photograph of the system is shown in figure 3.

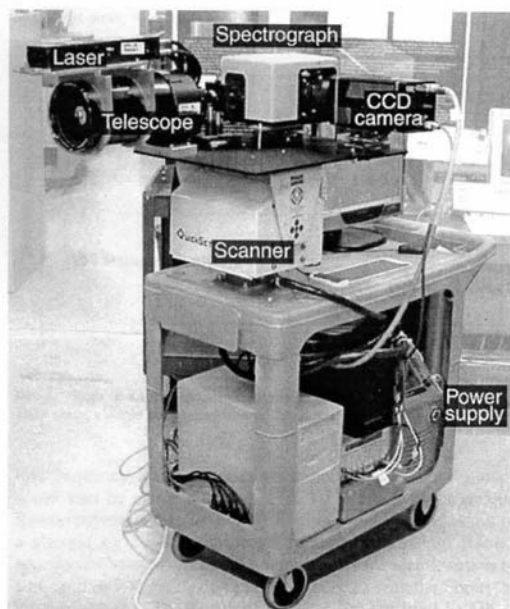


Figure 3. A photograph of the remote Raman spectroscopy system at the University of Hawaii (From Ref. 2).

In order to obtain measurements in high-background conditions without introducing excessive noise to the spectrum, the remote Raman system utilizes a pulsed laser and a gated detector.²⁻⁴ This combination allows the CCD to integrate only for the duration of the laser pulse, while Raman scattered photons are present. Therefore, the CCD is disabled during periods when there are no Raman scattered signal being generated and only background radiation is present.

In order to form the spectrum, the remote Raman system uses either a spectrograph, or an acousto-optic tunable filter (AOTF).³ The spectrograph uses a grating to disperse the collected signal into its spectral components. The AOTF is a tunable filter that uses a radio frequency generated acoustic wave in an anisotropic crystal to diffract a selected wavelength.³

The schematic diagrams of the spectrograph-based and AOTF-based

systems are shown in figure 4.³ The advantage of the AOTF-based system is its smaller size and less number of components, as the spectrograph is quite bulky and contained several optics that may misalign and miscalibrate the system.

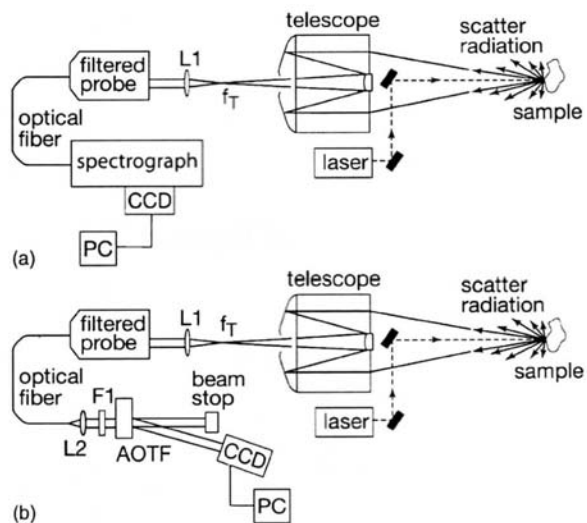


Figure 4. Schematic diagram of the (a) spectrograph-based and (b) AOTF-based remote Raman spectroscopy system (From Ref. 3).

The remote Raman system has been demonstrated to obtain Raman spectrum at distances of up to 100 meters.⁴ In addition, it has also been tested to obtain a spectrum using only a single laser pulse at a distance of 10 meters.²

A sample spectrum obtained with the remote Raman system is shown in figure 5.² These spectra were obtained using only a single laser pulse, with a distance of 10 m, and with room lights turned on. It can be seen from graph that the strong sharp peaks corresponding to the fingerprint Raman lines of these minerals can be observed with just one laser pulse or about 8 ns.

The remote Raman system can be used for remotely identifying both inorganic and organic materials during daytime or nighttime.

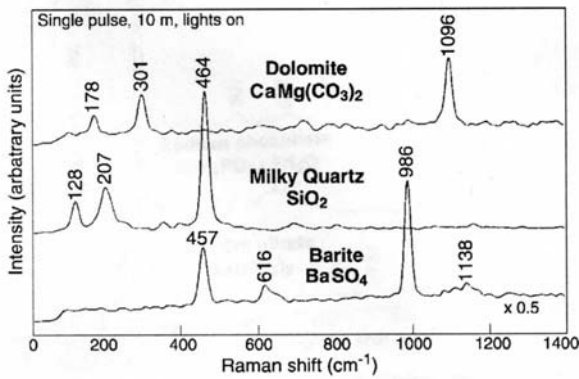


Figure 5. Spectra obtained using the remote Raman spectroscopy system.

Remote Raman Sensor System at NASA Langley Research Center

A remote Raman sensor system was developed at NASA Langley Research Center (LaRC) in collaboration with the University of Hawaii.⁵ This system utilizes a pulsed laser as an excitation source, a telescope for collecting backscattered signal, a spectrograph equipped with a notch filter to form the spectrum and attenuate Rayleigh scattered signal, and an intensified CCD camera to view the spectrum. A schematic diagram of the system is shown in figure 6.

The excitation source is a mini Nd:YAG pulsed laser source (model UltraCFR, Big Sky Laser, 532 nm, 45 mJ/pulse, 20 Hz, pulse width 8 ns). Using two 45° prisms, the laser beam is made collinear with the telescope's optical axis. This configuration, referred to as a coaxial geometry, permits scattered light to be gathered from the target for the 180° back scattering geometry to achieve maximum performance.

The laser beam hits the sample placed at 5.6 meters from the telescope, and the Raman scattered signal is collected by the telescope (Meade ETX-105, Maksutov-Cassegrain telescope with 4" aperture).

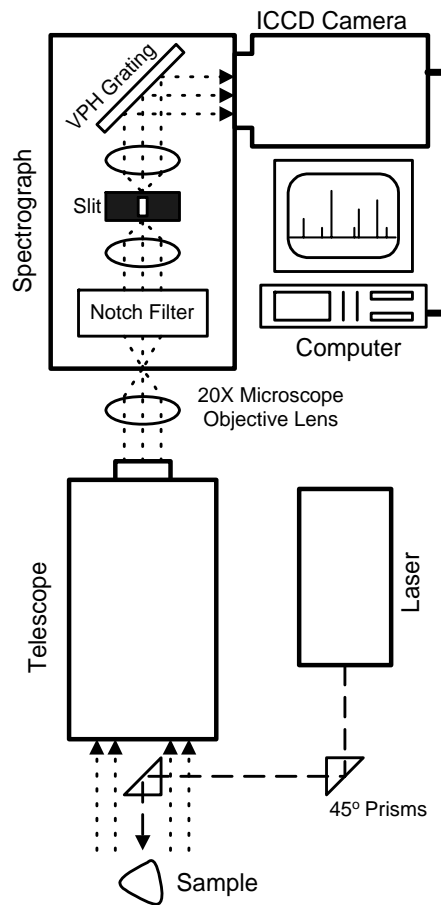


Figure 6. Schematic diagram of the remote pulsed laser Raman spectroscopy system (From Ref. 5).

The output from the telescope is directly coupled to the spectrograph (Kaiser Optical Systems, Inc. HoloSpec f/1.8i) through a 20x microscope objective lens. Inside the spectrograph, the input signal is first passed through a notch filter (Kaiser 532 nm Holographic SuperNotch-Plus Filter) to eliminate the strong Rayleigh scattered photons, then through a 100 μm slit to improve resolution of the spectra, and finally through a holographic transmission grating (Kaiser VPH Transmission Grating) to decompose the signal into its spectral components. The chosen width of the internal slit in the spectrograph corresponds to a spectral resolution of 4 cm⁻¹.

The spectrograph output is detected by thermoelectrically cooled and gated intensified CCD (ICCD) camera (Princeton Instruments PI-MAX Camera, 1024 x 256 ICCD, 26x26 μm^2 pixel size). The ICCD detects very weak stokes line by adding a gain of up to 250 to the input signal. This is implemented by first passing the input light signal through a photocathode that releases electrons from incident photons. The electrons are then accelerated through microchannel plates (MCP) where they are amplified as they hit the channel walls. An electron that hit the MCP walls generate additional electrons, which in turn hit the walls and generate more electrons, resulting in high gain of electrons. The electrons leaving the MCP strike the phosphor coating on a fluorescent screen causing it to release photons, which fall on the pixels of the CCD and generate charge.

The spectrograph grating simultaneously disperses two spectral tracks onto the CCD, with low frequency portion of the spectra on the upper half region of the CCD and high frequency portion on the lower half region. This innovative scheme dramatically improves the resolution of the spectrograph. The camera is operated using a manufacturer-supplied software (Winspec32), which is installed in the computer connected to the camera.

Vertical binning or summing of the signals in each column of pixels of the CCD was performed to produce single channel signal. The Raman spectrum is formed by plotting the binned signal versus channel or column numbers.

To obtain Raman spectra in lighted or high background conditions, the signal-to-background ratio is improved by gating the ICCD camera. The ICCD detector can be operated in either continuous or gated mode. In continuous mode, the detector is "on" and collects light during the entire

exposure time. This mode of operation is not practical for lighted measurements because it allows background signal such as mercury line from room lights to be recorded on the spectra. In the gated mode, the detector is "on" only for a very short period of time. This ensures that the camera only collects light whenever the laser strikes the sample. This short period during which the camera collects light is equal to the gate width multiplied by the number of laser pulses within the integration time. For our measurements, the gate width is set to 2 μs , and the laser pulse rate is 20 Hz. During an integration time of 1s, the detector is only on for 40 μs ; therefore, the duration for which the background radiation is picked up by the detector in the gated mode is only 1/25,000 of that in continuous mode. The data presented in this paper were collected with 10s integration time, corresponding to merely 400 μs of total duration that the detector is "on."

By using a pulsed laser, the intensity of the very weak Raman signal is increased, improving the ability of the system to detect it. The laser pulse width is only 8 ns, and within this very short period, the sample is hit by a large number of incident photons and Raman photons are generated. This results in significant improvement of the ratio of Raman photons to background photons during that short time interval.

A sample spectrum obtained from the NASA LaRC remote Raman sensor is shown in figure 7.⁵ These spectra were taken with a gate width of 2 μs with 200 accumulations at 20 Hz, equivalent to 10 s integration time.

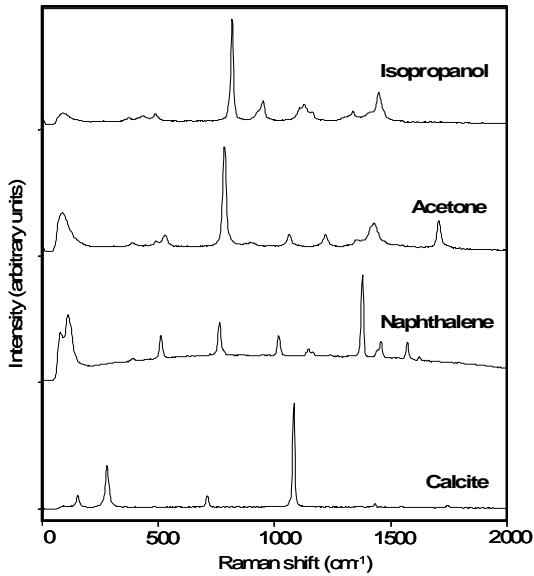


Figure 3. Raman spectra of Isopropanol, Acetone, Naphthalene, and Calcite (From Ref. 5).

The pulsed remote Raman sensor system at NASA LaRC demonstrated its ability to effectively obtain Raman spectra of ice, water and hydrous minerals. This system can therefore be utilized to detect presence of water or ice, which is essential in proving the existence of extinct or extant life on other planets.⁵ In order to make the system suitable for application in planetary exploration, it has to be made portable, ultra compact, and have low power consumption.

SUMMARY

Three different Raman spectroscopy systems designed for exploration of planetary surfaces were discussed. The Mars microbeam Raman spectrometer at the University of St. Louis is designed for close-up measurements of samples via a probe. The remote Raman spectroscopy system at the University of Hawaii is designed for remote measurement at distances of up to 100 m even in high background environments, or using a single laser pulse at a distance of 10 m. The

remote Raman sensor system at NASA LaRC is also designed to obtain measurements at a distance of the order of several meters. Its ability to detect water and ice and hydrous minerals has been tested.

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