Available online at www.sciencedirect.com
SCIENCE DIRECT®
Spectrochimica Acta Part A 59 (2003) 2391–2407
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Stand-off Raman spectroscopic detection of minerals on planetary surfaces

Shiv K. Sharma *, Paul G. Lucey, Manash Ghosh, Hugh W. Hubble, Keith A. Horton

Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., HIG, Honolulu, HI 96822, USA

Received 20 June 2002; accepted 15 August 2002

Abstract

We have designed and developed two breadboard versions of stand-off Raman spectroscopic systems for landers based on a 5-in. Maksutov–Cassegrain telescope and a small (4-in. diameter) Newtonian telescope receiver. These systems are capable of measuring the Raman spectra of minerals located at a distance of 4.5–66 m from the telescope. Both continuous wave (CW) Ar-ion and frequency doubled Nd:YAG (532 nm) pulsed (20 Hz) lasers are used as excitation sources for measuring remote Raman spectra of rocks and minerals. We have also made complementary measurements on the same rock samples with a micro-Raman system in 180 and 135° geometry for evaluating the system performance and for estimating effect of grain size and laser-induced heating on the spectra of minerals using α-quartz as a model mineral. A field portable remote pulsed Raman spectroscopic system based on the 5-in. telescope and an *f*/2.2 spectrograph has been developed and tested. We have also demonstrated a prototype of a combined Raman and laser-induced breakdown spectroscopy (LIBS) system, capable of providing major element composition and mineralogical information on both biogenic and inorganic minerals at a distance of 10 m from the receiver.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Raman; LIBS instrument; Mineral detection; Planetary surface; Mars

1. Introduction

Advancements in lasers, spectrographs and holographic optical components have made laser based techniques such as Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) effective tools for analyzing natural and synthetic materials. Advanced Raman spectroscopic techniques have been employed to investigate the mineralogy of meteorites [1–3], and have been proposed for in situ mineral characterization on planetary surfaces [4,5]. Both micro-Raman and remote Raman systems are being considered for

* Corresponding author. Tel.: +1-808-956-8476; fax: +1-808-956-3188.
E-mail address: sksharma@mano.soest.hawaii.edu (S.K. Sharma).

1386-1425/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S1386-1425(03)00080-5

future exploration on planetary surfaces [6–10]. The feasibility of using stand-off LIBS technique, which is based on detection of atomic emission lines of cations and other species in the laser generated plasma, has been demonstrated for the rapid online determination of the major and minor constituents of mineral drill core samples as well as for space applications [11,12].

Raman spectroscopy, which is based on inelastic scattering of light and provides information about molecular vibrations, offers molecular specificity, structural discernment and relatively simple spectral fingerprints. Advanced Raman techniques are finding increasing applications in a large variety of problems in earth and planetary sciences (e.g. [13–15]), including high pressure mineralogy [13,15–18], shock metamorphism (e.g. [19]), graphatization of carboneous matter in metamorphic rocks [20], fluid inclusions in minerals (e.g. [21,22]), pigments in ancient paintings [23], manuscript and other artifacts [24,25], biogenic minerals [26,27] and biomolecules (e.g. [28]). Of interest to the geologic community, and particularly for planetary exploration, is the possibility to unambiguously identify various minerals on planetary surfaces by their characteristic Raman peaks [6,29,30]. Most of the current applications in earth and planetary science are based on the micro-Raman and FT-Raman spectroscopic techniques. Raman spectroscopy can also be conducted with a telescope from a stand-off distance. Performance of remote Raman analysis has been explored theoretically by T. Hirschfeld [31], while the potential of measuring Raman spectra of organic materials [32], minerals, and inorganic materials with a small telescope and CW laser have been realized [8,9]. Raman lidars based on high power lasers and large telescopes have been used for investigating gaseous species in the atmosphere (e.g. [33,34]). Raman analyses of solid, liquids and gases have been performed at ranges of 500 m using a medium power UV laser with large collecting optics [35]. Recently, the feasibility of analyzing rocks and minerals with remote Raman spectroscopy at sample distances of 10s of meters from the receiver telescope has been demonstrated using modest diameter telescopes, modern efficient spectrometers, and low power lasers similar to those which have already flown on planetary missions [10,36,37].

Landers and rovers are an increasingly important element of NASA's solar system exploration program. Lander and rover sample analysis instrumentation includes methods requiring either close physical contact with a sample such as X-ray fluorescence (XRF) spectroscopy, or even sample acquisition, such as thermal analysis or mass spectrometry. There are inherent limitations to these techniques and limits to their performance at their present state of development. Visible, near-infrared, and thermal infrared spectroscopy of minerals and compounds all suffer from broad overlapping spectral features which complicate interpretation of their spectra. Sample selection is accomplished using imaging supported by multispectral or remote spectroscopic analysis. The recent experience with Sojourner/Pathfinder emphasized the importance of sample selection, as contact analyses are intensive in time or other resources. The ability to determine which samples within the region may be of specific interest without driving the rover to the various samples can reduce power consumption and risk significantly.

It is the broad, overlapping nature of mineral or chemical spectral features that constitute most of the challenge to interpretation of reflectance or emission spectra. In contrast, Raman spectra of minerals and mineral mixtures exhibit narrow and largely non-overlapping features, which are much more easily identified and separated. This capability enables rapid and model-independent mineralogical analysis of rocks and soils in the vicinity of a lander or a large rover. This stand-off Raman capability does not replace passive remote spectral analysis, which can survey much larger areas in less time, but does offer an entirely new ability to make less ambiguous mineralogical identification.

This paper critically reviews the stand-off Raman systems developed at the University of Hawaii in terms of balancing versatility against the physical limitations required for planetary exploration. We have measured Raman spectra of dozens of rocks and minerals, water and ice, as

well as of gaseous species in the atmosphere from distances ranging up to 66 m [8,10]

2. Instrumentation

In the following sections, we briefly describe prototypes of laboratory and field stand-off Raman spectroscopic systems as well as a combined stand-off Raman and LIBS system developed in our laboratory for detecting minerals and ices on planetary surfaces.

2.1. A stand-off pulsed Raman spectroscopic laboratory prototype

The experimental setup for our stand-off pulsed Raman system for measuring spectra of minerals and rocks in the laboratory as well as outdoors is schematically shown in Fig. 1. This SOPRS prototype system consists of a telescope (Meade ETX-125 Maksutov-Cassegrain, 125 mm clear aperture, 1900 mm focal length, *f*/15), a frequency doubled mini Nd:YAG laser source (Model ULTRA CFR, Big Sky Laser, 532 nm, 20 Hz), and a 0.25 m spectrograph (Spex Model 270M with 1800 grooves per mm grating, blazed at 500 nm)

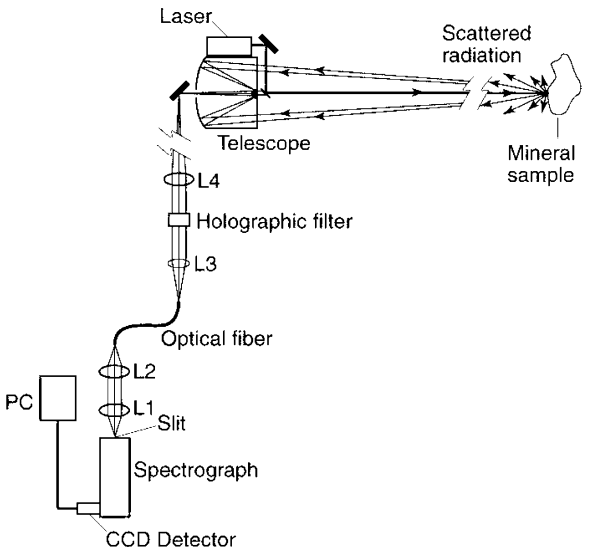

Fig. 1. Schematic diagram of a stand-off pulsed-Raman spectroscopic system developed at the University of Hawaii.

equipped with a gated intensified detector (Princeton Instruments Inc. Model I-MAX-1024-E). The maximum power of the laser at 532 nm is 35 mJ per pulse, the width of the laser pulse is approximately 8-nanosecond (ns), and the beam divergence is less than 8-milliradian (mrad). The spectrometer has entrance aperture ratio of *f*/4 and produces an image magnification of 1.23 at the exit. Grating position and slits of the spectrometer can be adjusted remotely with a hand held electronic controller.

In the ETX-125 telescope receiver, light enters through a multi-coated meniscus lens, proceeds to an *f*/2.2 primary mirror, and then to a convex secondary mirror (diameter 39.4 mm, 9.6% obstruction) that multiplies effective focal length by a factor of 6.8. The use of an oversized 138 mm diameter primary mirror results in a fully illuminated (unvignetted) field of view significantly wider than can be obtained with Maksutov optics incorporating primary mirrors of the same apertures as their correcting lenses. Raman measurements at distances ranging from 10 to 66 m were accomplished by focusing the telescope on the sample. The size of the Spex 270 M spectrometer is 43 (L) × 35 (W) × 20 cm (H), where L, W, and H, respectively, refer to length, width, and height of this instrument.

The laser is mounted on the side of the telescope and two 45° small fused quartz glass prisms are used to bring the beam to the center of the telescope to make it a co-axial system (Fig. 1). The main advantage of this arrangement is to get the maximum performance by gathering scattered light from the target in the 180° (backscattering) geometry while providing the ability to scan the telescope with a two-axis scanning motor.

The telescope is coupled to the spectrograph with a multi-mode fused-quartz optical fiber (200 μm in diameter). A lens (L4) collimates the light from the output of the telescope (see Fig. 1). A holographic super-notch filter was inserted between the collimating lens L4 and a 10 × microscope objective (L3). The L3 lens focuses the scattered light onto the optical fiber. The filter was adjusted to attenuate the elastically scattered and diffuse reflected laser light. The light leaving the optical fiber is collected and collimated by the

L2 lens (Fig. 1). The objective lens L1 focuses the light at the entrance slit of the Spex 270M imaging spectrograph. The spectrograph has a unique Czerny–Turner configuration for optical correction that provides for exceptional imaging capabilities. The system delivers near perfect spectral imaging over an area 25 wide × 12 mm high in the spectrograph image plane. Raman spectra were recorded with a thermoelectrically cooled gated and intensified CCD detector. The CCD array is 1024 × 256 pixels and each pixel is 26 × 26 μm^2. The detector is mounted in such a way that the Raman spectrum is dispersed along the horizontal (longer) axis. The signal in the 256 vertical pixels is binned to produce a single channel signal. Under certain cases, the horizontal pixels were also binned in a group of 2- or 3-pixels as one channel to improve signal to noise ratio (SNR). A plot of binned signal versus channel numbers formed the Raman spectrum. The spectra were calibrated to Raman shifts in cm^{-1}. Typical slit widths for Raman spectral measurements were 200 μm corresponding to resolution of 12 cm^{-1}. With slit widths of 400 μm, the Raman spectra of hydrous minerals with good S/N ratio in the O H stretching region were obtained [10]. It should be mentioned here that horizontal binning of the CCD pixels in a group of 2- or 3-pixels does not affect the position (frequency) of the Raman bands but it does increase the S/N and lower the spectral resolution.

Two commercial computer programs were used for data collection and reduction with the pulsed remote Raman system. Princeton Instruments WINSPEC 32-bit Windows software package from Roper Scientific was used for spectral data acquisition from the intensified and gated CCD detector. With this software, data can be acquired both in imaging and spectral mode. Further processing of the spectral data was carried out using GRAMS/32 software package from Galactic Industries.

2.2. A field-portable stand-off pulsed Raman spectroscopic system

The field-portable remote pulsed Raman spectroscopy system (Fig. 2) is based on the same

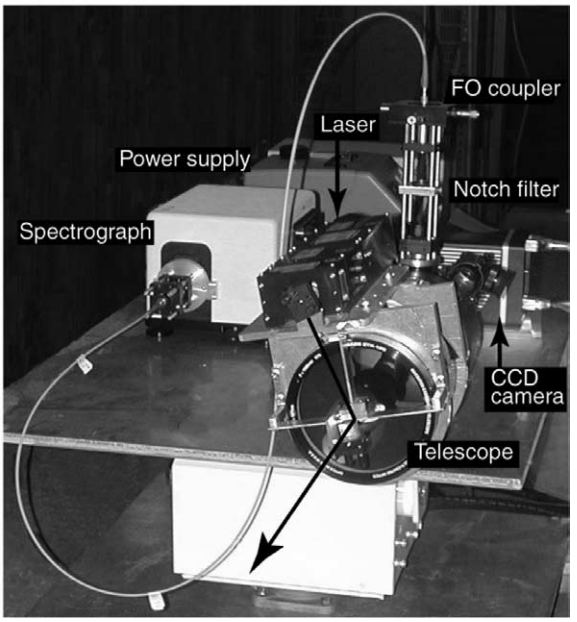

Fig. 2. Photograph of the University of Hawaii's field-portable stand-off pulsed Raman spectroscopic system.

design as the pulsed Raman laboratory prototype described in Section 2.1 above except that we have incorporated a smaller and more efficient (*f*/2.2) spectrograph (HoloSpec *f*/2.2, Kaiser Optical Systems, Inc.). The multi-element lenses used in the *f*/2.2 holographic axial transmitting imaging spectrograph collect light over a solid angle many times larger than that of Czerny–Turner spectrographs, which operate usually in the range *f*/3.3–*f*/11. The larger solid angle, coupled with the high (80%) diffraction efficiency of the volume holographic transmission grating, results in a greatly improved light throughput (at least by a factor of 4 as compared with the throughput of a *f*/4 spectrograph for the same size of the entrance slit). The size of the HoloSpec spectrometer is 17 (*L*) × 22 (*W*) × 16.5 cm (*H*) that is approximately five times smaller in volume than the Spex 270 M spectrograph. Further reduction in the size of this instrument is possible by optimizing it with the rest of the remote Raman system. The HoloSpec has a volume holographic transmission (HoloPlex) grating optimized for Raman spectroscopy with 532-nm laser excitation. For our gated CCD detector with 1024 × 256 pixels, the grating has a

spectral band pass of 86.7 nm or 2610 cm^{-1} Stokes–Raman shifted from 532 nm laser wavelength. Since the wide spectral range of the window, the linear spectral dispersion of the system varies monotonically from 0.08 nm $pixel^{-1}$ (2.8 cm^{-1} $pixel^{-1}$) at the low-wavelength end to 0.06 nm $pixel^{-1}$ (1.5 cm^{-1} $pixel^{-1}$) at the high wavelength end. This spectrograph has no moving parts and uses slits of fixed widths (50, 165, 250 μm) that require physically changing the slits when needed. With a slit of 50 μm width, good quality stand-off Raman spectra of silicates were obtained with medium resolution. A high throughput slit up to 250 μm was used for measuring the Raman spectra of glasses or gaseous species at 10 m distance from the telescope.

2.3. A continuous wave telescopic Raman spectroscopic system

A laboratory version of the telescopic Raman spectroscopy system has been designed and assembled using continuous wave (CW) laser excitation (Fig. 3). The Raman spectra recorded with the CW laser and remote Raman system were relatively easy to compare with the Raman spectra of the same minerals and rocks recorded with our multichannel micro-Raman system (for details see

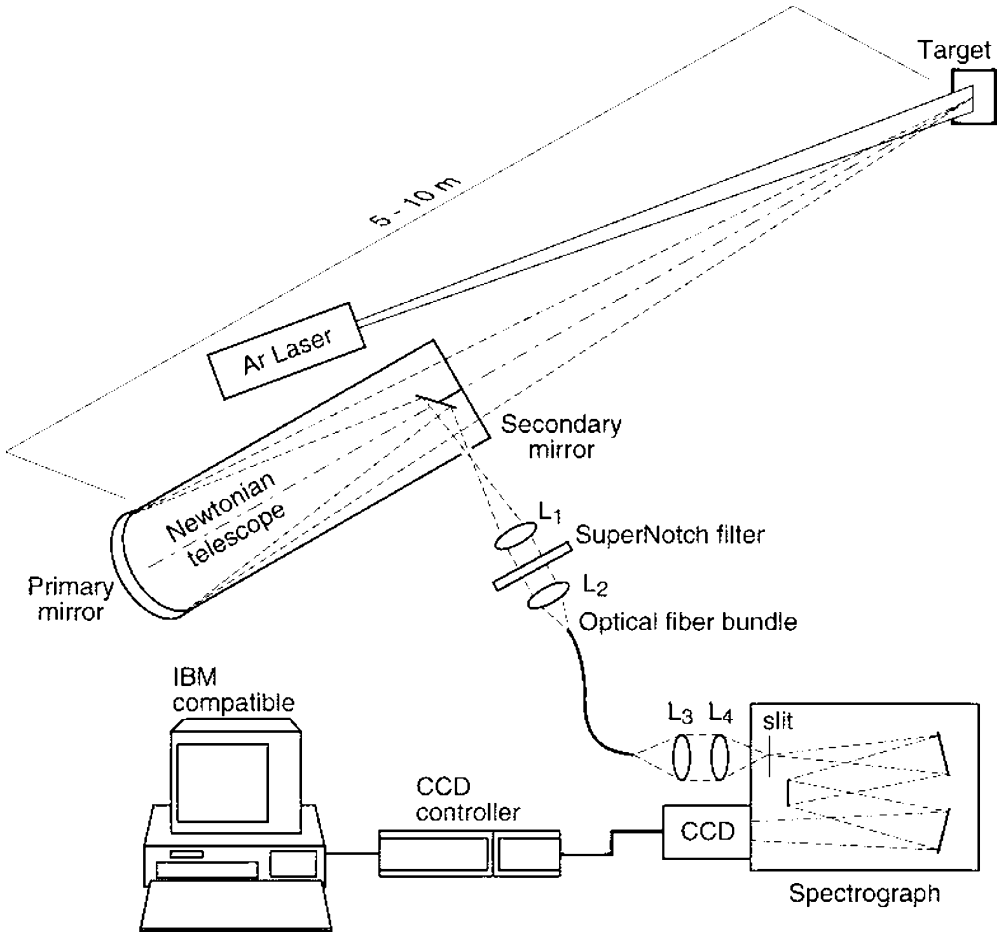

Fig. 3. Schematic diagram of a CW telescopic Raman spectroscopic system developed at the University of Hawaii.

ref. [38]) as both these systems use CW lasers as excitation sources and the oblique geometry shown in Fig. 3.

The bench top telescopic Raman system consists of a Spectra Physics Ar-ion laser (Model 165) operated at 488 nm, a 1/4 m imaging spectrograph (CVI Digikrom model DK240, f/3.9, focal length 240 mm, 1200 g mm^{-1} grating), a liquid nitrogen cooled Photometrics CCD imager (1024×256 pixels), a 10.8 cm diameter f/4.2 portable Newtonian telescope, and a data collection computer. The telescope primary is a 44.5 cm focal length parabolic mirror with clear aperture of 10.5 cm. An optical fiber bundle, which is formed into a linear fiber array at one end, is used to connect the telescope to the spectrograph. The linear fiber array of 25, 50-μm fibers acts as the spectrograph slit dispersing the received light across the entire CCD array. This arrangement of optical fibers helps in increasing the light input into the spectrograph and in matching the f-number of the spectrometer with the fiber bundle. A holographic super notch filter (Fig. 3) is adjusted to attenuate the elastically (Rayleigh) scattered and reflected laser light at 488 nm. The CVI spectrograph has a computer controlled, curved entrance slit. The slit width of the spectrograph can be changed from 10 to 3000 μm as well as the slit height can be selected from 2 to 20 mm. The spectrometer has maximum resolution of 0.06 nm with 1200 g mm^{-1} grating. The stray light in the spectrograph is less than 0.01% at 220 nm wavelength and even lower in the visible part of the spectrum. The size of this commercial spectrometer is 55 (L) $\times$ 24 (W) $\times$ 12 cm (H).

The laser and telescope are at an oblique angle but were focused upon the same sample spot at a distance of 4.8 m from the telescope primary mirror. This geometry minimizes the amount of reflected laser light from the sample surface reaching the telescope. The CCD is cooled to 168 K with liquid nitrogen. Various combinations of laser power and integration time intervals were investigated to derive a reasonable compromise of SNR and data acquisition efficiency. Current nominal operating specifications are: 130 mW laser power at the sample and 60 s integration for light colored samples and 180 s integration for dark samples. The system was moved into a larger laboratory that allowed collecting remote Raman data at 9–10 m from the sample.

2.4. A combined stand-off LIBS and pulsed Raman spectroscopic (LIBS/Raman) system

As mentioned in the Section 1, LIBS has been proposed for space exploration. We have explored the use of LIBS combined with pulsed-laser Raman spectroscopy for mineral analysis at a distance of 10 m. We modified our remote pulsed Raman system to collect LIBS data, thus obtaining quantitative values for cation composition in our samples. By analyzing the cation information collected in the LIBS experiment alongside the anion information provided by Raman scattering, a more complete image of the mineral's structure and composition can be obtained.

Fig. 4 shows a schematic representation of the experimental setup for the stand-off LIBS/Raman experiment. A Q-switched Nd:YAG laser (Model DCR-2, from Spectra-Physics, 1064 nm, 20 Hz), operating at 200 mJ per pulse, was focused on the sample approximately 10 m away creating a plasma spark. The telescope is placed beside the

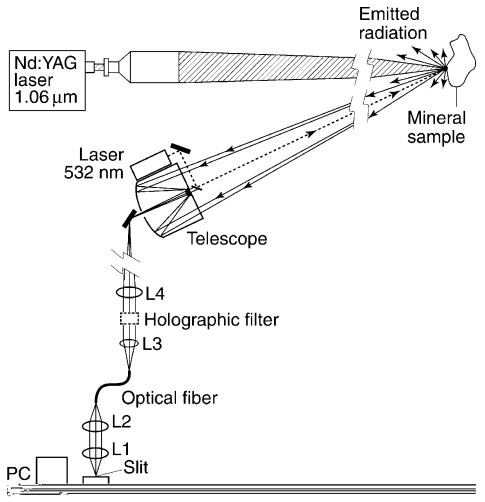

Fig. 4. Schematic representation of the stand-off LIBS/Raman set up.