Pulsed remote Raman system for daytime measurements of mineral spectra

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Abstract

A remote Raman system has been developed utilizing a 532 nm pulsed laser and gated intensified charged couple device (ICCD) detector in the oblique geometry. When the system is set for 50 m sample distance it is capable of measuring Raman spectra of minerals located at distances in the range of 10–65 m from the telescope. Both daytime and nighttime operations are feasible and the spectra of minerals can be measured in a short period of time, of the order of a few seconds. In oblique geometry, measured sampling depth is more than 30 m, during which the system maintains very high performance without any adjustments. Much longer sampling depth (0.1–120 m) has been observed when the system is configured in the coaxial geometry. Clear advantages of using a gated detection mode over the continuous (CW) mode of operation in reducing the background signal and eliminating long-lived fluorescence signals from the Raman spectra are presented. The performance of the pulsed Raman system is demonstrated by measuring spectra of Raman standards including benzene (C6H6) and naphthalene (C10H8), a low Raman cross section silicate mineral muscovite (KAl2(Si3Al)O10(OH)2), and a medium Raman cross section mineral calcite (CaCO3).

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1. Introduction

Most of the Raman spectroscopic systems used for mineral analysis use continuous wave (CW) laser sources that do not require gated detectors for measurement [e.g., 1–4]. A limited number of Raman measurements of minerals and silicate melt at high temperature with pulsed laser excitation and gated detection is also available in the literature [e.g., 5]. The commercial Raman systems have been designed for analyzing samples in the research labs in the dark or under low light illumination. These Raman instruments are in general equipped with CW laser sources for exciting samples. This trend is mainly the result of difficulty in measuring Raman signals due to the inherently weak Raman cross section of various materials. With the development of compact lasers, smaller and more efficient CCDs and spectrographs, Raman systems are finding new applications as smaller portable systems that are being used for exciting work in the field of remote sensing. It is now possible to take a portable Raman system to the field and analyze chemicals and minerals on site in a short period of time. Previously reported portable remote Raman systems developed by various groups with CW lasers [e.g., 6, 7] were tested in the dark and data could only be collected if the background radiation was low. Although these measurements in the dark or during night are suitable for many applications, one needs a remote Raman system, which can be used at anytime, day or night. Such day and nighttime remote Raman systems will be suitable for analyzing chemical spills, fume clouds, toxic explosions in real time, and will not be limited by the background. For geological applications, daytime measurements will be helpful in visibly locating interesting minerals, analyzing them and finally collecting them without taking the extra risk of haz-

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ardous navigation over rocks, cracks, bushes, pot holes, wild animals, etc. encountered during night missions.

We have recently developed a pulsed remote Raman system that is capable of measuring Raman spectra of minerals in daylight, as well as during night, at distances in the range of 10 cm to 120 m. An earlier portable remote Raman system developed at the University of Hawaii and elsewhere [6–8] mostly utilized 180° scattering geometry, and frequently used optical-fiber-based coupling of the telescope with the Raman spectrometer. These optical-fiber-based systems using a single 500 μm diameter fiber are designed to work in adverse conditions, such as that on Mars where it would be desirable to separate the spectograph and detector from the telescope. Optical fiber coupling, however, does reduce the efficiency of the remote Raman system due to small size of the fiber. In such a system one must carefully align the components so that most of the collected scattered light can enter the single fiber. A slight misalignment in the system significantly reduces the Raman signal. The extra optical components needed for collimating and directing the beam into the fiber also reduce the signal because of reflection losses from each added interface. Fiber-based coupling of the Raman receiver with the spectrograph also limits the sampling depth to one meter. With the development of smaller spectrometers, it is now possible to directly couple the telescope to spectrometer and detector and mount the whole system on a 3D scanner. The new setup that we have developed has a compact design and totally eliminates the fiber and optical loss associated with the fiber coupling.

2. System description

Fig. 1 shows the schematics of the pulsed remote Raman system in two configurations (a) coaxial geometry, and (b) oblique geometry. In the coaxial monostatic system, the laser beam is made collinear with the telescope’s optical axis by using two 45° prisms. In the oblique mode the laser is directly aimed at the distant target and the telescope collects the scattered radiation at an oblique angle that is mainly determined by the sample distance from the Raman system (typically less than 1°). The pulsed remote Raman system consists of a 127 mm telescope (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−1, 20 Hz, pulse width 8 ns, beam divergence 0.5 mrad), a Kaiser F22-2 Holospac spectrometer equipped with a gated thermo-electrically cooled CCD detector. The telescope is directly coupled to the spectrometer through a 20× (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.

Since the Raman cross sections are inherent properties of the materials and are fairly low in values, the design of a remote Raman system for daytime measurement is based on improving the Raman signal-to-background ratio. For the daytime measurements of Raman spectra, the system requires two critical features, namely (1) a pulsed laser and (2) a gated detector. A pulsed gated system significantly improves the signal-to-noise ratio and successfully measures Raman spectra in daylight from samples located 50 m away from the system. The CCD detector of the pulsed remote Raman system can be operated in two modes (a) continuous wave (CW) mode and (b) gated mode. In the CW mode, the detector is “on” for duration equal to the integration time and records everything during this period. In the gated mode, the detector is “on” only for a very short period of time (equal to gate width times number of laser pulses within the integration period). So, for an integration time of 1 s, the detector in gated mode is only “on” for 20 μs for our system, which is set for gate width of 1 μs and the laser has a pulse rate of 20 Hz. Hence, the duration for which the background radiation is picked up by the detector in the gated mode is reduced by a factor of 50,000 in comparison to the CW mode. It is further possible to improve on the system performance by reducing the gate width. Since the pulse width of our laser is only 8 ns and the time constant of Raman scattering is of the order of 10−13 s, one would expect to receive all the Raman photons within a few nanoseconds-time interval. Hence, effectively one could use a much shorter gate width of the order of 10 ns.

In order to increase the intensity of the Raman signal, a pulsed laser is used. A 35 mJ pulse−1 green laser (20 Hz) provides 700 mW of average power. More importantly, the target is hit by a large number of incident photons within a short period of 8 ns (pulse width). As a result the Raman photons are generated within that 8 ns. This significantly improves the
ratio of Raman photons to background photons during that short time interval. Our high-power pulsed laser is suitable for measuring samples that do not have significant absorption at the laser wavelength. For geological applications, our 532 nm laser wavelength in the remote Raman system was found suitable for measuring various minerals and compounds such as calcite, magnesite, dolomite, barite, anhydrite, gypsum, mica, quartz, borosilicates, plagioclase, microcline, ice, water, carbon dioxide, dry ice, gas hydrates, nitrogen, oxygen, methane, benzene, cyclohexane, acetone, methanol, xylene, hydrocarbons, high explosive (HMX, TATB), etc. [9,10].

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.

3. Samples

For evaluating the performance of the stand-off Raman systems, analytical grade benzene and naphthalene samples were used as Raman standards. For measurements at a distance of about 10 m, the benzene sample was contained in a glass bottle of 3 cm diameter and 6.5 cm high. Polycrystalline naphthalene was contained in the 3 cm diameter glass bottle similar to that used for the benzene sample. The rock-forming mineral samples were purchased from Ward’s Natural Science Establishment, Inc., Rochester, New York. These samples were used without any polishing or cutting. The muscovite mica sample was from Bihar, India, and the polycrystalline translucent crystal of calcite was from Mexico. Unpolarized Raman spectra of these samples were measured in nearly back scattering geometry except the mica sample that was placed at 30° to the laser beam to avoid strong background in the low-frequency spectral region due to strong reflection of 532 nm laser light by the sample.

4. Results and discussion

Fig. 2 illustrates the benefit of using a pulsed remote Raman system in gated mode over the CW mode. All unpolarized spectra were collected in the lab with a calcite sample placed at a distance of 10 m from the fiber-coupled remote Raman system, with an integration time of 1 s and single accumulation. When the system is operated in the continuous mode and with lab lights on, the detector picks up (i) a large amount of background white light and (ii) the mercury emission lines of the tube lights, as shown in Fig. 2(a). The strong mercury emission lines disappear when the lab lights are turned off and a significant reduction in the background is observed as shown in Fig. 2(b). However, background still contains long-lived fluorescence signal produced by the impurities in the calcite crystal. When the system is operated in the gated mode the background signal becomes low even with all the lights turned on in the laboratory. As shown in Fig. 2(c), the detector in gated mode effectively minimizes the strong fluorescence background and mercury lines from the spectra. The similar relative intensities of the calcite peaks in all three plots indicate that most of the Raman photons were collected by the detector within the gate width of 1 ms. Alternatively, one could set the proper gate parameters (trigger and gate width) by observing the intensities of the Raman lines.

With the use of a pulsed laser and a gated detecting system we have successfully measured the Raman spectra of several minerals [9] in the labs with all lights on.

Fig. 3 compares the performance of the oblique remote Raman system to that of coaxial remote Raman systems; fiber coupled and directly coupled. The use of prisms in the coaxial systems does create back reflection of the laser beam as well as backscattering in the near field of the telescope, which results in some loss of laser power at the target. Such problems are avoided in the oblique arrangement where the laser is directly aimed at the target and the scattered signal is collected at a small angle from the laser beam. In order to evaluate the performance of the system, a sample of benzene was placed.
at 9 m distance from the telescope. The data were collected in the laboratory with all room lights on with integration time of 1 s. Fig. 3a compares the Raman spectra of benzene measured with the fiber-based coaxial monostatic system to that measured with a directly coupled coaxial monostatic system (see Fig. 3b). The data clearly show improvement by a factor of 10 in the performance of the direct-coupled system relative to that of the FO-coupled remote Raman system. This improvement is largely due to elimination of losses associated with the fiber and associated optics. As shown in Fig. 3c, further improvement by a factor of 1.6 in the performance of the remote Raman system is observed in the oblique design, relative to directly coupled coaxial system, where power losses associated with the reflection and scattering from prisms in the near field are avoided. Eliminating the near-field scattering also reduces the intensity of the baseline close to the laser line and helps in detecting low-frequency Raman bands. As can be seen from the Raman spectrum of naphthalene (Fig. 4), it is possible to measure low-frequency Raman lines down to 76 cm$^{-1}$ with the oblique geometry setup. The low-frequency Raman spectrum of naphthalene in Fig. 4 is comparable to that reported previously [11]. This remote Raman spectrum was measured from a distance of 10 m with 50% of maximum laser power (i.e., 17.5 mJ pulse$^{-1}$), an integration time of 0.2 s, and five accumulations in gated mode with all the laboratory lights on.

With the improvement in the performance of the remote Raman system, it is now possible to measure Raman spectra of colored minerals and darker rocks as well as of silicate minerals that have weak Raman cross sections. Fig. 5 shows the Raman spectra of muscovite mica from a distance of 10 m with integration time of 5–60 s with the lab lights on. Muscovite is a weak Raman scatterer, and the sample is 6 mm thick (8.5 cm $\times$ 6.5 cm $\times$ 0.6 cm). Measurement of muscovite’s Raman spectrum is quite difficult, especially from a distance of 10 m. It can be seen from Fig. 5 that even with 5 s integration time, spectral fingerprints of muscovite at 260, 417 and 701 cm$^{-1}$ are clearly visible in addition to the atmospheric oxygen and nitrogen Raman lines at 1556 and 2331 cm$^{-1}$, respectively (Fig. 5, bottom curve). Within ±2 cm$^{-1}$ the frequencies of these major muscovite Raman lines in the remote Raman spectrum are found to be in agreement with those reported in the literature and in the Caltech Raman database [12,13]. McKown et al. [12] have carried out detailed vibrational analysis of muscovite, a dioctahedral mica. According to these authors, the Raman and IR-active modes calculated at frequencies greater than 800 cm$^{-1}$ are dominated by internal sheet TiO$_2$ stretching and Ti–O–Ti bending motions, where T are cations in tetrahedral coordination (T = Si, Al). The vibrational modes in the 800 and 360 cm$^{-1}$ range have internal tetrahedral sheet motions mixed with K and octahedral Al displacements. Modes at frequencies less than 360 cm$^{-1}$ have lattice and OH motions [12]. It is found that the inter-sheet bonding in the muscovite structure can affect modes at frequencies as high as 824 cm$^{-1}$ [12]. A relatively strong band at 701 cm$^{-1}$ corresponds to symmetric stretching of the bridging oxygen,
Fig. 6. Raman spectra of calcite measured from 50 m distance during daylight using oblique geometry in gated mode. Laser: 532 nm, 35 mJ pulse$^{-1}$, 20 Hz; slit 100 μm, 10 s integration time.

ν(T-O-T) mode. The background in the top spectrum in Fig. 5 is in part due to short-lived sample fluorescence, and partly to the background room lights.

There are significant differences in the background radiation observed between the well-illuminated laboratory and outdoor daytime field environments. Under the laboratory condition, all light sources were powered by a 60 Hz line. Apart from sinusoidal fluctuations in the intensity, lab light also contains strong emission lines from a mercury source.

The background radiation in the outdoor experiments is much stronger in intensities and is continuous in nature. In order to verify the effectiveness of gated remote Raman system for measuring minerals in daylight we performed outdoor measurements in the evening under clear sky (1 h before the sunset). Fig. 6 shows the Raman spectra of a calcite sample at a distance of 50 m from the remote Raman system in gated mode (integration time = 10 s; spectral resolution, 9 cm$^{-1}$; slit width, 100 μm; gate width, 1 μs). The Raman active symmetric stretching bands of oxygen (1556 cm$^{-1}$) and nitrogen (2331 cm$^{-1}$) from the atmosphere are clearly detected above the background, along with lattice and internal modes of calcite Raman bands at 282, 711, 1085, 1434, and 1748 cm$^{-1}$ [2,14]. The 156 cm$^{-1}$ lattice mode in this set of experiments was purposely blocked to avoid accidental exposure of CCD by laser light during assembling and alignment of the system in our first trial for daytime measurement. The contribution from the continuous solar radiation towards the background can be seen in the baseline of the spectra. Fig. 7 shows the daytime Raman spectra of a 100 ml of benzene sample placed at 50 m from the system with integration time of only 1 s. With a 100 μm slit, weak doublets associated with the $e_g$ ring stretching modes at 1585 and 1606 cm$^{-1}$ are clearly resolved along with a strong 992 cm$^{-1}$ breathing mode of the benzene ring. Presence of atmospheric nitrogen, oxygen and broad solar background can also be seen in the Fig. 7 spectrum. Another advantage of the remote Raman system operating in the gated mode is that there are few cosmic rays observed due to short operation time. All spectra presented in this paper are shown as as-observed and no cosmic ray correction or baseline adjustment is made. It is important to point out that the system is not blocking cosmic rays. Due to short on-time of the detector (of the order of few μs) in the gated mode, the probability of capturing a cosmic ray is reduced dramatically. The ability of a gated ICCD to clean the register just before accumulating data is also an important feature for our remote Raman system designed for daytime measurements.

For field applications of remote Raman spectroscopy, one of the demanding features is the ability of the system to measure Raman spectra of samples at various distances without any focusing adjustments. A desirable remote Raman system should have a large sampling depth without any significant degradation of the performance. The sampling depth in a coaxial system is expected to be much larger than that of the oblique configuration because of crossover of the laser beam in the field of view of the telescope in the oblique geometry. The sampling depth for our oblique remote Raman system was measured by (i) setting the system for detecting mineral spectra from a distance of 50 m, and (ii) simply placing the target at various positions, without making any other adjustment to the system. Fig. 8 shows the variation in the

Fig. 7. Raman spectra of benzene at 50 m distance measured during daylight using oblique geometry with integration time of 1 s in gated mode. Laser: 532 nm, 35 mJ pulse$^{-1}$, 20 Hz; slit 100 μm.

Fig. 8. Intensity of calcite 1085 cm$^{-1}$ line vs. sample distance showing sampling depth of remote Raman system in the oblique geometry in gated mode. Laser: 532 nm, 35 mJ pulse$^{-1}$, 20 Hz; slit 100 μm, 10 s integration time.
intensity of 1085 cm\(^{-1}\) Raman line of symmetric stretching mode of carbonate ions of calcite sample as a function of sample distance in meters.

It is evident from Fig. 8 that the oblique remote Raman system does maintain high signal intensity between 20 and 50 m but the signal is detected at 10 and 65 m. The variation in the intensity counts of the 1085 cm\(^{-1}\), \(\nu_1\), band of \(\text{CO}_3^{2-}\) ion for a fixed sample distance in Fig. 8 is mainly due to fluctuations in the laser power of our pulsed laser source. The aperture of the 20× microscopic lens, and laser beam going beyond the field of view of the telescope in the oblique geometry mainly limits the sampling depth. With a coaxial system one does maintain a large sampling depth, as laser beam is always in the field of view of the telescope. Recently, we have tested our pulsed gated remote Raman system in the coaxial geometry, and have collected high-quality Raman spectra up to 120 m. The system showed good performance with a large sampling depth from 10 cm to 120 m. Ability to make measurements without refocusing the Raman receiver is an important feature for a Raman instrument suitable for landers or rovers as it minimizes adjustable mechanical parts.

Fig. 9 shows the Raman spectra of calcite measured from distances of 60 and 90 m in the daytime using the coaxial geometry. At 60 m distance all the calcite bands including the low-frequency lattice mode at 156 cm\(^{-1}\) could be easily detected. Raman signals from the atmospheric gases, e.g. nitrogen (at 2331 cm\(^{-1}\)) and oxygen (at 1556 cm\(^{-1}\)) could also be easily observed. The broad low-frequency Raman band at 109 cm\(^{-1}\) is most likely unresolved rotational Raman bands associated with the atmospheric gases. At 90 m distance, the Raman peaks from the atmosphere show larger intensities in comparison to spectra shown at 60 m distance, simply due to increased path length of laser beam in the atmosphere. The peaks associated with calcite also dropped in intensity, mainly as a result of the smaller solid angle suspended by the telescope at 90 m and the decrease in the intensity because of scattering and divergence of the incident laser beam. Because of strong wind conditions on the day of the experiment, there were also signal fluctuations associated with the vibration of the system. Our calcite sample is only 8.5 cm \(\times\) 5.5 cm \(\times\) 2.5 cm in size and small vibrations due to gusts picked up by the instrument make the laser beam (which is about 3.5 cm in size at 90 m) partially miss the target. Since the laser beam is always in the field of view of the telescope in the coaxial geometry, small signal fluctuation associated with mechanical vibration would be of no concern if the target is large. Future remote Raman systems aiming for much larger ranges and smaller targets would have to address the issues associated with beam divergence and vibrational stability of the system.

5. Conclusion

We have recently developed a directly coupled oblique remote Raman system for planetary applications, which has a compact design, high performance, large sampling depth, and capability of measuring minerals at 90 m distance under daylight condition. It is possible to further improve the system performance by enclosing the system, optimizing the gating parameters, utilizing lasers with higher pulse rates, and optimizing on ICCD parameters such as detector temperature and amplifier gain. A further improvement in the system performance would translate directly into acceptance of smaller telescopes and future development of compact remote Raman systems with superior performance.

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