Raman spectroscopy on Mars: identification of geological and bio-geological signatures in Martian analogues using miniaturized Raman spectrometers

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The first Raman spectrometers to be used for in situ analysis of planetary material will be launched as part of powerful, rover-based analytical laboratories within the next 6 years. There are a number of significant challenges associated with building spectrometers for space applications, including limited volume, power and mass budgets, the need to operate in harsh environments and the need to operate independently and intelligently for long periods of time (due to communication limitations). Here, we give an overview of the technical capabilities of the Raman instruments planned for future planetary missions and give a review of the preparatory work being pursued to ensure that such instruments are operated successfully and optimally. This includes analysis of extremophile samples containing pigments associated with biological processes, synthetic materials which incorporate biological material within a mineral matrix, planetary analogues containing low levels of reduced carbon and samples coated with desert varnish that incorporate both geo-markers and biomarkers. We discuss the scientific importance of each sample type and the challenges...
using portable/flight-prototype instrumentation. We also report on technical development work undertaken to enable the next generation of Raman instruments to reach higher levels of sensitivity and operational efficiency.

1. Introduction

(a) Planetary exploration

Significant progress in understanding the composition and physical processes associated with the surface of Mars has been made in the last decade, thanks largely to the successful deployment of sophisticated orbiters, landers and rovers equipped with advanced, analytical instrumentation [1–6]. A number of remote sensing techniques have been used in the exploration of Mars. In particular, remote infrared spectrometry of the Martian surface has played a key role in the mapping of the distribution of minerals [7–10] and past water [11,12], laser altimetry has been used to produce high-resolution topographic maps [13] and subsurface radar has provided data on the stratigraphy and water content of the Martian subsurface [14,15]. Various in situ measurement techniques have been used to provide additional data on the geochemistry of Mars. These include laser-induced breakdown spectroscopy (LIBS) [16,17], X-ray powder diffraction and X-ray fluorescence spectroscopy [18] for elemental information and gas chromatography-mass spectrometry for molecular identification and isotopic analysis [19]. In recent years, further advances in instrument technologies, such as the miniaturization, qualification and robustness of optics, lasers and detector systems have led to the prospect of Raman spectrometers also becoming a key component in the analytical suites proposed for the next generation of planetary rovers. Two major future missions which have placed a high priority on the acquisition of Raman spectra are described below.

(b) The ExoMars mission

The ExoMars (exobiology on Mars) mission is part of ESA’s ongoing Aurora programme to develop the skills and technology required to facilitate manned missions to Mars. The first part of the programme involves the development of a rover equipped with a highly capable analytical laboratory. The rover offers two assets previously not exploited on Mars: a drill capable of retrieving samples from up to 2 m below the surface and a Raman laser spectrometer (RLS) for analysing the molecular composition of samples. The RLS instrument is a compact, rugged, low-power and low mass Raman spectrometer mounted in the science instrument chain on the Sample Preparation and Delivery System (SPDS) inside the rover’s analytical suite. The SPDS delivers a crushed sample from the Martian regolith to the instrument, which can identify many biological and mineralogical materials without preparation, contact or destruction. The sample can then be passed to the other instruments in the analytical suite after identifying organic material or minerals of interest. Organic molecules are not expected to survive on top of the Martian regolith due to solar UV radiation sterilizing the surface [20] and producing abundant oxidizing chemical species [21]. Therefore, the ExoMars rover’s 2 m drill is of great significance as it offers the first chance to retrieve samples from those parts of the regolith most likely to contain life or remnants of life [22–24].

The RLS instrument uses a DPSS continuous laser excitation source at 532 nm, focused into a 50 µm spot on the target sample with a total irradiance of not more than 0.6–1.2 kW cm$^{-2}$ [25]. The optical head is fibre-coupled to the rest of the instrument with a fibre diameter of 50 µm, imaged 1:1 by the spectrometer. The spectrometer incorporates a holographic transmission grating which disperses a single diffraction order between 100 and 4000 cm$^{-1}$ onto a thermoelectrically cooled, charge coupled device (CCD) detector. The CCD is a thin-gate, back-illuminated, 4-phase, non-inverted mode $528 \times 2048$, 15 µm pixel CCD230 manufactured by e2v technologies [26]. A conceptual sketch of the instrument subsystems is shown in figure 1.
Figure 1. Elements of a Raman spectrometer representative of the ExoMars RLS flight instrument design.

Spectral acquisition times are anticipated to be in the range 0.1–60 s and the use of suitable CCD operating modes (and given the full well capacity of the detector pixels and anticipated instrument noise levels) will deliver a dynamic range of $10^3$–$10^4$ for intense Raman bands (dynamic ranges of more than $10^4$ have been demonstrated on flight-representative instruments). The camera will be driven by a mature flight-qualified electronics package with significant space heritage [27,28]. The system is supplied by the Rutherford Appleton Laboratories in the UK and is based around a custom ASIC which digitizes the analogue video signal from the CCD by correlated double sampling. Drive signals are programmable with flexible operating modes and the system is compatible with low-power, radiation hardened CCDs. A detector operating temperature of between $-10$°C and $-40$°C is maintained to guarantee SNR performance at the anticipated end-of-life radiation dose.

The overall science goals of the instrument are to

— search for signs of extinct or existing life,
— perform analyses of soil and rocks at surface and subsurface,
— determine the chemistry, mineralogy and origin of surface, and
— characterize water and geochemical distribution as a function of depth in the subsurface.

Consequently, some of the key aspects of spectrometer performance that are of significant scientific interest are

— its ability to acquire signatures from biological pigments at very low concentration levels (within mineral matrices),
— its ability to detect ancient carbon at low concentration levels,
— the ability to use the Raman spectra obtained from samples containing reduced carbon to determine the thermal history of the material, and
— to determine whether or not biotically and abiotically produced carbon can be distinguished using Raman spectra obtained from the sample.

(c) NASA Mars 2020 mission

In addition to the RLS instrument due to launch as part of the ExoMars analytical laboratory in 2018 [29], a high-resolution spectrometer is likely to be included in the NASA Mars 2020 payload [30,31]. The rover mission follows on and benefits from the technologies developed for the highly successful MSL rover and will be an integral step towards future sample return missions. Its primary aims will be to evaluate the geological environment on Mars in order to assess the planets past habitability and the potential preservation of biosignatures [31]. Raman spectroscopy has been identified [30] as a potentially powerful tool for both the study of fine-scale mineralogy and the detection of organic and reduced carbon [31].

In order to demonstrate the full range of capabilities and technical readiness of such instrumentation a number of prototype Raman instruments have been developed and tested. One
example is the micro-beam Raman spectrometer (MMRS). Developed by Washington University and the Jet Propulsion Laboratory, MMRS is a science payload instrument designed for landed Mars missions [32] capable of close-up analysis of rocks and soils on the planetary surface [33]. The instrument probe head is deployed by a robotic arm [34] and a stepper motor inside the optical head can scan through a range of 10 mm across a sample surface. Using a low-power mode, 10 mW, 532 nm laser [33], Raman spectra are acquired from 100 to 200 spots across surface during a 1–4 h period [32,33]. The system will cover spectral ranges of 200–1800 cm$^{-1}$ and 2500–4000 cm$^{-1}$ to accommodate for the detection of minerals and graphitic carbon as well as organic molecules and water [33]. The instrument achieves a precision of less than 2 cm$^{-1}$ for peak positions and has a spectral resolution of approximately 7 cm$^{-1}$. In 2004, MMRS was ranked Category One in the MSL payload selection [35], but further development to improve its science capability and Technology Readiness Level has given rise to a Compact Integral Raman system (CIRS). CIRS shares a similar architecture to MMRS (minus the use of an optical fibre [36]) and will be capable of satisfying the current 2020 mission goals related to context and fine-scale mineralogy [32].

2. Raman analysis of geological and astrobiologically relevant samples

A major factor in the successful design and operation of any scientific instrument developed for a space mission is the identification of appropriate analogue samples that can be used to inform instrument design, inform the development of instrument operating modes and verify the performance of the instrument (in terms of its ability to answer the fundamental science goals of the mission). In particular, it is important to ensure that an adequate range of challenging datasets (sample types) is defined at an early stage and that blind analyses are performed in order to demonstrate the full capability of the instrument (i.e. to ensure that optimum operating modes and sampling strategies are sufficiently developed and that sensitivity levels are fully understood and optimized). To this end, and given the science goals of the ExoMars and NASA Mars 2020 missions, a number of sample sets are identified here that can be used to verify and optimize the capabilities of miniaturized Raman spectrometers. These sample sets include pigments known to be associated with biological processes, planetary analogues containing reduced carbon and geological samples coated with desert varnish. The following sections describe the specific importance of each of these sample types and identify the key parameters and spectral features that need to be measured. Examples of the data acquired with prototype instrumentation are also included.

(a) Detection of low concentration biosignatures in mineral matrices

A range of synthetic samples have been prepared to investigate the ability of a flight-representative instrument to detect organic signatures within a mineral matrix [37,38]. The sample set consisted of powdered calcite, gypsum, dolomite and aragonite containing varying concentrations by mass of β-carotene, glycine and toluene, prepared using a ball mill. Figure 2 shows one example, where the Raman spectrum of glycine can be seen superimposed on the gypsum matrix (the concentration of glycine was 0.1% by mass). It should be noted that these data have not been processed except for extracting the spectra from the CCD image; no background subtraction or smoothing has been performed. For these tests, a commercial equivalent of the RLS flight detector was cooled to the RLS operating temperature of −10°C and coupled to a commercial spectrograph and optical head. The spectrograph incorporated a transmission VPH grating, consistent with the flight design and the optical head and 532 nm laser were selected and operated in accordance with the flight operating mode (50 µm spot size, laser power less than 100 mW).

In addition to the synthetic samples described above, a number of natural samples (incorporating pigments associated with biological processes) have also been identified (and recovered) that are considered to be suitable for characterizing and verifying the performance of
Figure 2. Example of Raman spectrum obtained from mix of glycine and gypsum (the concentration of glycine was 0.1% by mass).

the prototype spectrometers. One example is stratified gypsum crust extracted from a hypersaline saltern evaporation pond in Eilat, Israel (see [39] in this volume for example spectra from these samples). The gypsum crust was found to contain microbial pigment, apparent in the form of three different coloured layers. Analysis of material from each of the different layers using a prototype instrument, confirms that it is possible to discern wavenumber differences for each of the bands associated with the carotenoid pigments (i.e. Raman bands between 1000 and 1515 cm\(^{-1}\)). Noting that, the wavenumber differences expected for each of the different colours is expected to be between 1 and 5 cm\(^{-1}\) based on laboratory studies [39].

Future studies of these materials should focus on identifying the lower level of sensitivity to biosignatures as a function of operating/sample scanning mode and sample grain size.

(b) Desert varnish

Desert varnish is a very thin skin of material, comprising iron(III) oxides, manganese (IV) oxides and clays, found on the outer surfaces of some rocks in desert locations [40]. The varnish is thought to be associated with bacterial or micro-colonial fungi activities and therefore provides an ideal combination of geological and biologically related components for testing the capabilities of Raman instrumentation.

Several samples of rock that appear to be coated with desert varnish were obtained from two separate locations in Death Valley, USA. Portable instruments (both 785 and 532 nm excitation) were used to obtain Raman spectra from several random positions on the surface of each sample, and this process was repeated on the interior of the rocks after breaking pieces off with a chisel. The spectra obtained indicate that most of the samples are composed of quartz/haematite. Other materials observed include plagioclase, albite, magnetite and goethite. Spectra obtained with the 532 nm instrument also indicate the presence of \(\beta\)-carotene. Current work [41] is focused on determining the range of operating modes (i.e. sampling points and exposure times) required to identify all of the different components in the samples and the sensitivity limit of each instrument design. Figure 3 shows a photograph of a rock found in Death Valley (USA) which is coated with desert varnish and a Raman spectrum acquired from one of the samples.
Figure 3. Photograph of an example sample that was found to be coated with desert varnish (the sample was located in Death Valley, California) and a Raman spectrum acquired from one of the varnish samples. (Online version in colour.)

(c) Reduced carbon

The idea that the structure of organic molecules may be probed and their exact nature determined by way of Raman spectroscopy is almost as old as the original demonstration of the Raman effect itself [42]. More recently, this has developed into the study of a wide range of carbonaceous materials using the technique, including carbon nanotubes [43–46] (for a comprehensive review of Raman spectroscopy of carbon nanotubes, refer to Dresselhaus et al. [47]), carbon films [48–50], laboratory samples of a variety of amorphous carbons [51] and geological carbon deposits [52–54]. Raman spectroscopy is ideally suited to the investigation of carbonaceous material due to the strong Raman cross section of particular carbon bond configurations, its ability to unambiguously distinguish between sp2 hybridized (graphite like) and sp3 hybridized (diamond-like) carbon [55] and the wealth of structural information which can be gleaned from detailed analysis of carbon spectra. The strong Raman cross section of certain carbon bond configurations also means that the technique is extremely sensitive to the presence of carbonaceous material, with concentrations as low as 0.08% having been detected with flight-like spectrometer prototypes [56].

Figure 4 shows an example Raman spectrum with bands indicative of the presence of reduced carbon that was acquired during previous work from a basaltic Mars analogue sample collected from a Late Ordovician (Caradoc) pillow lava exposure on the coast near Helen’s Bay, Northern Ireland [57]. The first-order Raman spectrum of carbon is dominated by the so-called D and G Raman bands, with Raman shifts of around 1350 cm$^{-1}$ and between 1580 and 1600 cm$^{-1}$, respectively [58]. The G band results from the relative motion of C atoms in sp2 bonded carbon and so can arise from long chain hydrocarbons as well as from perfect graphite, whereas the D band is caused by excitation of the breathing mode of aromatic rings and is therefore forbidden in perfect graphite (see fig. 4 of [58] and accompanying explanation). This has led to the association of the D band with disorder and indeed, the intensity ratios $I_D/I_G$ and $I_D/(I_D + I_G)$ have, under certain circumstances, been shown to correlate with other metrics of disorder such as H/C atomic ratio and in plane crystallite size, $La$ [54], as well as the thermal maturity of the sample. In the specific case of a space mission, however, it is necessary to identify the parameters which can provide scientifically significant information, but are computationally simple to measure. The background reduction processes required to reliably calculate the intensity ratios given above may be beyond the capabilities of the on-board (instrument) processor on a rover or lander, so alternative parameters must be found. It has been demonstrated that careful measurement of the
The width and exact position of the carbon G band can yield additional information about the thermal maturity of a carbon sample and that these parameters can be used to differentiate between distinct carbon populations of differing thermal maturity, both distributed across a geological region [56] and in a single rock sample [57], using instrumentation similar to that developed for the ExoMars mission.

One of the primary scientific objectives of the current generation of planetary exploration missions is to search for signs of either extant or extinct life [30,59]. Given the harsh present-day conditions on Mars, any such evidence found is likely to be in the form of fossilized remnants of ancient life [60], the most probable indicator of which will be deposits of reduced, or sp2 hybridized carbon. There are however a number of abiotic sources of reduced carbon, including meteoritic infall [61] and volcanic activity [62]. The suitability of Raman spectroscopy for the detection and characterization of such deposited carbon has already been discussed, however, it is also clear that the biogenicity of a particular population of carbon cannot be determined by Raman spectroscopy alone [55,63,64]. Nevertheless, the detection of abiotic reduced carbon on an extra-terrestrial planetary surface, such as that of Mars, would be a valuable result in itself. Carbon could act as a metabolic feedstock for microbial life, and therefore, its presence in an environment could be an indicator of a viable habitat, highlighting a region which should be investigated more closely using any other instruments which a particular lander or rover has at its disposal [57,65].

Future studies of samples that contain reduced carbon (using flight-like prototype instruments) should focus on the development of sampling strategies that optimize the overall sensitivity level and verify/improve the determination of thermal history using computationally simple analysis of the parameters extracted from the spectrum.

3. Discussion

The development of Raman instrumentation for future planetary applications is likely to focus on the appropriate selection/combination of excitation wavelengths (for the specific science goals of a particular mission), the manufacture and qualification of robust and reliable lasers (that are
stable and have low mass and high power), the development of dual instruments which combine complementary analytical techniques (e.g. providing simultaneous information on the elemental and molecular composition of a sample) and the development of high performance input optics such as stand-off systems, which are capable of sampling materials at remote distances from the rover/lander (enabling rapid and efficient identification of surface regions that should be targeted by rovers for more detailed investigation).

(a) Instrument design

The selection of an optimum excitation wavelength (which can broadly be broken down into red, green and UV options), for a specific set of mission science goals, depends on a number of factors. While the wavenumber shift of a particular Raman band is (broadly) independent of the excitation wavelength, the scattering intensity is inversely proportional to the excitation wavelength, i.e. a Raman spectrum obtained using an ultraviolet excitation source is nearly 300 times stronger than that obtained with near infrared excitation source, allowing for the detection of weaker spectral features [66]. However, when using a green excitation source, for example, the emission of fluorescence from a sample can be significantly larger (compared with the absence of florescence when using a red wavelength source). This fluorescence emission can overwhelm the Raman signal, especially the weaker bands generated by organic molecules which have low-energy electronic states [66]. By contrast, the use of a UV excitation source can discriminate the Raman bands in the UV from the fluorescence that occurs at visible wavelengths [67]. However, a shorter excitation wavelength increases the irradiance of the incident laser beam at the sample, increasing the chances of thermal degradation [68].

Often when studying biomarkers, it is beneficial to take advantage of the resonance Raman effect. Careful selection of the excitation wavelength can produce enhanced Raman bands corresponding to vibrational modes occurring in the chromophore; a region of localized electronic transitions [69]. The addition of electronic transitions can enhance a Raman signal by a factor of $10^3$–$10^6$, and thereby, allow the analysis of molecules in significantly low concentrations ($10^{-4}$–$10^{-6}$ M) [69]. A 524–532 nm excitation source often coincides with the absorption band of carotenoids (such as scytonemin and $\beta$-carotene) leading to a more rapid and conclusive detection [70–72]. However, it should be noted that pigments such as chlorophyll and red-coloured minerals, such as iron (III) oxides are not observed with visible excitation wavelengths at all, but can be identified using a 785 nm excitation [70]. In addition, ultraviolet excitation wavelengths can promote the observation of biological compounds such as proteins and DNA compounds. These compounds often exhibit strong fluorescence in the visible wavelength region, but their strong absorption of UV wavelengths means the resonance Raman effect can aid their detection, even in dilute solutions [67].

(b) Stand-off Raman

Currently, the ability of a rover to acquire spectra from a broad range of locations within its immediate environment is limited by the need to either, move and manipulate a full collection optics/spectrometer system or to extract a sample from the surface and transfer it to the location of the spectrometer. However, the possibility of performing Raman spectroscopy at significant stand-off distances enables a much more efficient approach to mission operations. Stand-off Raman spectroscopy is already a well-established technique for terrestrial applications (e.g. in the fields of geology and mineralogy) and for the past decade, efforts have been focused upon adapting and miniaturizing the instrumentation so that it can be used for planetary exploration [73]. Through the use of gated detectors and pulsed lasers (which, in combination, significantly reduce noise from ambient light and fluorescence) and telescopic optics [73–75], Raman analysis has been successfully performed at distances of over 120 m from the sample, in high level, ambient light conditions (i.e. outside, during daylight) [74]. The retrieval of information from a remote distance not only removes the need for rover relocation (saving time, power and other resources)
but also allows the exploration of what would normally be inaccessible regions of a planet [35].
In fact, in addition to the prospect of deploying a stand-off Raman instrument on Mars, a recent Science Definition Report has identified Raman analysis as a key element in the exploration of Europa [76], and it is reported that a stand-off Raman instrument, similar to existing prototypes, would be capable of measuring and identifying various salts, organic and CO₂ ice on the surface of Europa, potentially to a depth of a few centimetres [77].

(c) Combined instrumentation

Another key aspect of future instrument development will be the development of highly mass/power efficient systems (i.e. low mass and low power) which provide dual functionality. For example, in recent years, efforts have been focused on developing a stand-off Raman/LIBS instrument [78,79]. LIBS is a complimentary technique that, unlike Raman, is sensitive to elemental composition and allows geochemical analysis of a sample [80]. The two systems share many common instrument components allowing for the integration of the two techniques into a single instrument [73]. As a technique, LIBS already has some space heritage [81] and a prototype combined (Raman+LIBS) system has already demonstrated its suitability for future planetary exploration missions [78,80]. In the light of NASA's future Mars2020 mission, it has recently been suggested that a combined Raman LIBS instrument, operating from the mast of a rover would be capable of probing remote samples, acting as either a reconnaissance tool or as a primary science instrument [80].

4. Conclusion

The miniaturized Raman spectrometers that are likely to be included in the next set of planetary rovers to be sent to Mars have been described and a range of sample sets have been identified that are being used to optimize and verify the performance of such flight instruments. An overview of a number of ongoing studies that use analogue samples to inform instrument design and operation have been highlighted—these include

— samples of desert varnish recovered from Death Valley, USA—which were found to contain: quartz, haematite, plagioclase, albite, magnetite, goethite and β-carotene using portable, flight-like spectrometers;
— synthetic samples containing biosignatures; where the capability was demonstrated to discern closely separated Raman bands and detect 0.1% concentration of organic signatures with a high signal-to-noise ratio using a flight-representative prototype;
— natural samples containing biosignatures; where the capability was demonstrated to discern adjacent Raman bands corresponding to carotenoid pigments in alternate layers of a colonized inorganic substrate; and
— basaltic Mars analogue samples containing—where the capability of flight-like, portable instruments to detect low concentration levels of reduced carbon and to distinguish between materials of differing thermal maturity was demonstrated.

The importance of each type of sample has been explained in terms of the key science requirements of current missions and the status of progress in these areas is reported.

Recommendations for the focus of future work (using such samples and flight-like prototypes) in preparation for the launch of the ESA/RosCosmos ExoMars mission and the NASA Mars2020 mission are also provided. Finally, an overview of the key instrumentation development activities that are currently being pursued in readiness for the next generation of planetary applications is given.

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