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**Development of an optimised detection
system for a stand-off Raman spectrometer
for planetary and lunar exploration.**

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Under the supervision of Ian Hutchinson at the University of Leicester.

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

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ABSTRACT

Raman spectroscopy is a chemical and molecular structural identification technique which is sensitive to the vibrational modes of molecules. It is used in many fields, including: pharmaceuticals, security/defence and nuclear waste. In the past decade, significant advances in the miniaturisation and robustness of key technologies have also led to the consideration of Raman spectroscopy for application in the field of planetary exploration and in 2020 the first Raman instruments will be launched as part of two missions to the surface of Mars. The first is ESA's ExoMars rover, which will include a compact macroscopic Raman instrument within its analytical laboratory. The second is NASA's Mars2020 mission which will feature a stand-off Raman spectrometer: an instrument that provides a method of retrieving molecular information from remote distances, enabling rovers to investigate otherwise inaccessible regions. However, current stand-off and in situ instrument designs are limited by the challenging resource constraints associated with deploying systems on rover platforms, resulting in the need for detailed system software models and instrument prototypes that enable complex trade-offs and optimisations to be performed.

This thesis presents work completed in preparation for the ExoMars, Mars2020 and other future planetary exploration missions that require information on molecular composition to fully address their science goals. It describes the development of sophisticated, end-to-end radiometric models and detailed software simulation tools for predicting and evaluating the performance of miniaturized Raman instrumentation. Details on the development of a prototype stand-off Raman instrument, designed to verify the software models are also provided, along with results from a number of instrument performance and model verification tests, including detector radiation damage campaigns. Several studies completed in order to assess and demonstrate the performance of various prototype and flight representative Raman instruments are also reported, including laboratory investigations of mission relevant sample standards and two field test campaigns.

For Kate. Because you were never given the chance.

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LIST OF ACRONYMS AND ABBREVIATIONS

ADC	Analogue to Digital Conversation/Converter
ADU	Analogue-to-Digital Units
AIMO	Advanced Inverted Mode Operation
APD	Avalanche Photodiode
APXS	Alpha Particle X-Ray Spectrometer
AR	Anti Reflective
AUPE	Aberystwyth University PanCam Emulator
CCD	Charge Coupled Device
CDS	Correlated Double Sampling
ChemCam	Chemistry & Camera
CIC	Clock Induced Charge
CIRS	Compact Integrated Raman Spectrometer
CLEP	Chinese Lunar Exploration Program
CLUPI	Close-Up Imager
CMOS	Complementary Metal-Oxide Semiconductor
CNSA	Chinese National Space Administration
COTS	Commercial Off-the-Shelf
CW	Continuous Wave
DAVINCI	Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging
DISR	Descent Imager/Spectral Radiometer
DN	Digital Number
DPSS	Diode Pumped Solid State
EDM	Entry, Descent and Landing Demonstrator Module

EJSM	Europa Jupiter System Mission
EMCCD	Electron Multiplication Charge Coupled Device
ESA	European Space Agency
FET	Field Effect Transistor
FWC	Full Well Capacity
FWHM	Full Width at Half Maximum
GCMS	Gas Chromatograph Mass Spectrometer
GRS	Gamma-Ray Spectrometer
HI-RISE	High Resolution Imaging Science Experiment
HRC	High Resolution Camera
iCCD	Intensified Charge Coupled Device
ICE	Instrument Control Environment
ICL	Israel Chemicals Ltd
InSAR	Interferometric Synthetic Aperture Radar
IR	Infrared
ISEM	Infrared Spectrometer for ExoMars
ISRU	In Situ Resource Utilisation
JPL	Jet Propulsion Laboratory
LDMS	Laser Desorption Mass Spectrometer
LED	Light Emitting Diode
LIBS	Laser Induced Breakdown Spectrometer
LIDAR	Light Detection and Ranging
Ma_MISS	Mars Multispectral Imager for Subsurface Studies
MAHLI	Mars Hand Lens Imager
MastCam	Mast Camera
MCP	Microchannel Plate

MER	Mars Exploration Rover
MINAR	Mine Analogue Research
MMRS	Mars Microbeam Raman Spectrometer
MOC	Mission Operations Centre
MOFSET	Metal Oxide Semiconductor Field Effect Transistor
MOMA	Mars Organic Molecular Analyser
MOXIE	Mars Oxygen In Situ Resource Utilisation Experiment
MSL	Mars Science Laboratory
MURFI	Mars Utah Robotic Field Investigations
NA	Numerical Aperture
NASA	National Aeronautics and Space Administration
ND	Neutral Density
Nd:YAG	Neodymium-Doped Yttrium Aluminium Garnet
NIMO	Non Inverted Mode Operation
OD	Output Drain
OG	Output Gate
OS	Output Source
PanCam	Panoramic Camera
PDA	Photodiode Array
PI	Principal Investigator
PIXL	Planetary Instrument for X-ray Lithochemistry
QE	Quantum Efficiency
RD	Reset Drain
RLS	Raman Laser Spectrometer

RMI	Remote Micro-Imager
RMS	Root Mean Square
Roscosmos	Russian Federal Space Agency
SA/SPaH	Sample Acquisition, Sample Processing, and Handling
SHERLOC	Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals
SNR	Signal-to-Noise
SOT	Science and Operation Team
SPDS	Sample Preparation and Distribution System
SSE	Solar System Exploration
STFC	Science & Technology Facilities Council
TDI	Time-Delayed Integration
TEC	Thermoelectric Cooler
TRL	Technology Readiness Level
TSSM	Titan-Saturn System Mission
UKSA	United Kingdom Space Agency
USGS	United States Geological Survey
UV	Ultraviolet
VERITAS	Venus Emissivity, Radio Science, InSAR, Topography, and Spectroscopy
WISDOM	Water Ice and Subsurface Deposit Observation On Mars
XRF	X-Ray Fluorescence

PUBLICATIONS

This section briefly describes each of the publications that I have contributed to during the PhD.

JOURNAL PUBLICATIONS

Culka, Adam, Kateřina Osterrothová, Ian Hutchinson, Richard Ingle, Melissa McHugh, Aharon Oren, Howell GM Edwards, and Jan Jehlička. "Detection of pigments of halophilic endoliths from gypsum: Raman portable instrument and European Space Agency's prototype analysis." Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 372, no. 2030 (2014): 20140203.

The work presented in this paper focused on colonised evaporitic material removed from the bottom of a saltern pond near Eilat, Israel. The material contains pigments called carotenoids (coloured organic compounds that play important roles in UV radiation screening and DNA repair in many living organisms) produced by different types of cyanobacteria. Due to their complexity, it can be difficult to differentiate between carotenoids using only Raman spectra. Carotenoid spectra were acquired with prototype instrumentation for a comparison between handheld field instruments and flight-representative instruments with the aim of distinguishing between different carotenoids. There is significant interest (i.e. with collaborators) in how the stand-off system will perform for these kinds of sample and the radiometric model/simulator has been used to illustrate the performance of the system.

Malherbe, Cedric., Richard Ingle, Ian B. Hutchinson, Melissa McHugh, Jan Jehlička, Howell G. M. Edwards. "Accurate differentiation of carotenoid pigments using flight representative Raman spectrometers" Analytical and bioanalytical chemistry.

Following on from the work completed by Culka et al, this body of work uses the RLS prototype and two flight-like handheld Raman spectrometers of different wavelengths. The work involves a detailed analysis of the stratified carotenoids mentioned previously. In order to evaluate the instruments' ability to distinguish between the different types of

carotenoid (which result from varying lengths of molecules), effort was focused on optimising the calibration of each system to demonstrate that the small variations in band position observed were not due to calibration errors.

Harris, Liam V., Melissa McHugh, Ian B. Hutchinson, Richard Ingle, Cédric Malherbe, John Parnell, Alison Olcott Marshall, and Howell GM Edwards. "Avoiding misidentification of bands in planetary Raman spectra." Journal of Raman Spectroscopy (2015).

This paper followed on from the work presented at GeoRaman. We highlight where confusion may occur when identifying the most useful bands for differentiation between molecules. Spectra were taken from a number of Mars analogue samples, including the Eilat samples mentioned previously. In order to differentiate between all of the target molecules presented, we recommended a particular spectral range and resolution for a Raman spectrometer.

Hutchinson, Ian B., Richard Ingle, Howell GM Edwards, Liam Harris, Melissa McHugh, Cedric Malherbe, and J. Parnell. "Raman spectroscopy on Mars: identification of geological and bio-geological signatures in Martian analogues using miniaturized Raman spectrometers." Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 372, no. 2030 (2014): 20140204.

Here we reviewed the technical capabilities of the Raman instruments planned for future planetary missions and detail the preparatory work being pursued to ensure that such instruments are operated successfully and optimally. The paper focuses on a range of scientifically important samples types and discusses the challenges of using flight-prototype instrumentation. The paper reports on the work undertaken to reach higher levels of sensitivity and operational efficiency in the next generation of Raman instruments.

CONFERENCE PUBLICATIONS

McHugh, M., I. B. Hutchinson, R. Ingley, N. Nelms, and H. G. M. Edwards. "Optimising the Operation and Performance of a Raman Spectroscopy Instrument Developed for Planetary Exploration Applications." LPI Contributions 1783 (2014): 5050.

I presented the work in an oral presentation at the 11th GeoRaman conference in 2014.

McHugh, M., Ian B. Hutchinson, Richard Ingley, Nick Nelms, Howell G.M. Edwards. (2015) Optimising the Performance of a Stand-Off Raman Spectroscopy Instrument for Planetary Exploration Applications. SciX Poster Abstract. Prize Awarded.

A poster that describes the development of a radiometric model for stand-off Raman instrumentation. The model was used to assess the theoretical performance of three separate instrument configurations for nine different sample/environment scenarios. We presented the signal-to-noise ratios achieved for a carefully selected set of samples which exhibit significantly different levels of fluorescence emission in low, medium and high levels of ambient light.

McHugh, M., Hutchinson, I. B., Ingley, R., & Nelms, N. (2016). Optimising the Operation and Performance of a Stand-Off Raman Instrument Developed for Planetary and Lunar Exploration. LPI Contributions, 1980.

Work I presented in an oral presentation at the 3rd International Workshop on Instrumentation for Planetary Mission, held 24-27 October, 2016 in Pasadena.

Harris, L.V., M. McHugh, I. B. Hutchinson, R. Ingley, J. Parnell, H. G. M. Edwards. "Detecting Reduced Carbon on Mars Using RLS: Raman Spectroscopy of Mars Analogues in Preparation for ExoMars." Last modified April 12, 2015.

A poster describing how the environment can alter the Raman spectrum of carbon and how this affects its analysis. The analysis was performed using flight-representative

instrumentation and is an example of how ambiguity within spectra can lead to the misidentification of bands and even an error in the characterisation of an instrument. This work will be critical in finalising the instrument requirements/operating modes for the stand-off system.

Ingley, R., I. Hutchinson, L. V. Harris, M. McHugh, H. G. M. Edwards, N. R. Waltham, P. Brown, and P. Pool. "Competitive and Mature CCD Imaging Systems for Planetary Raman Spectrometers." LPI Contributions 1783 (2014): 5066.

A description of the camera system (performance and operation) for the Raman Laser Spectrometer (including the detector and frontend electronics) developed by academic and industrial partners in the UK. The work also reports on the ongoing activities surrounding the verification and optimisation of the overall instrument performance are also included.

Hutchinson, I. B., H. G. M. Edwards, R. Ingley, L. Harris, M. McHugh, C. Malherbe, J. Jehlicka, C. Marshall, and J. Parnell. "Preparations for the Launch of the EXOMARS Raman Laser Spectrometer---A Review of Recent Studies Which Highlight the Astrobiological and Geological Capabilities of Portable Raman Instrumentation." LPI Contributions 1783 (2014): 5093.

This work describes analysis performed on a variety of analogue and real world samples using flight representative systems in various operating modes and environmental conditions to prepare for mission operations and to optimize/demonstrate the capabilities of each instrument configuration.

Wang, A., Lambert, J.L., Hutchinson, I., Monacos, S., McHugh, M., Wei, J. and Yan, Y.C., 2016. Two High Performance In Situ Raman Spectrometers for Landed Planetary Missions. LPI Contributions, 1980.

A review of the Compact Integrated Raman Spectrometer and the Mars Microbeam Raman Spectrometer. The oral presentation commented on the status of both instruments and presented the latest TRL for the systems.

Lerman, H. N., Hutchinson, I. B., Bannister, N. P., McHugh, M., Ingle, R., Lester, M. & Garton, D. (2016). The Development of a Highly Integrated Imaging Payload for Space Weather and Maritime Monitoring. IPM Contributions, 2016.

A poster presenting the development of a UV camera system for a space weather monitoring CubeSat payload.

PERSONAL CONTRIBUTIONS

Chapter 1

All work in this chapter is my own and is included after discussions with supervisors.

Chapter 2

All work in this chapter is my own and is included after discussions with supervisors.

Chapter 3

All work in this chapter is my own and is included after discussions with supervisors.

Chapter 4

Radiometric simulations were based on low level code developed by I.B. Hutchinson.

Chapter 5

Radiation campaign funded by UKSA and ESA. Eilat samples provided by J. Gehlicka.

Chapter 6

For section 6.1, the instruments and samples were provided by J.L.Lambert (JPL) and data was acquired by A.Wang. Analysis was performed by M. McHugh and I.B. Hutchinson

For section 6.2, Instruments provided by F.Rull. Data was acquired by G Lopez-Reyes and M. McHugh. Sample Was provided by J. Parnell.

Chapter 7

Field Trips were funded by UKSA and the Centre for Astrobiology. MINAR: data was acquired by M. McHugh, I.B. Hutchinson, L.V. Harris and P. Edwards. Data was analysed by M. McHugh and I.B. Hutchinson

PREFACE

The work produced for this thesis has contributed to two ongoing international space instrument development programmes: ESA's ExoMars Raman Laser Spectrometer and the NASA JPL CIRS instrument. Major outputs of the work include:

- (i) Modelling, development and build of a prototype stand-off Raman instrument (suitable for future planetary exploration missions);
- (ii) Instrument control software & camera system for a prototype in situ Raman instrument;
- (iii) Participation in proposals for instruments on the NASA Mars2020 mission;
- (iv) An end-to-end software simulator that models every aspect of a Raman spectrometer instrument (including pixel level detector operations, radiation damage, optics & grating performance, laser emission and sample properties);
- (v) Simulations that have been used to inform instrument proposals and the optimisation of existing prototype instruments;
- (vi) Collaborative activities with the UK nuclear waste and mining industries;
- (vii) Collaborative activities the UK instrument/camera manufacturers;
- (viii) Analysis of several different planetary analogue materials with prototype, instrumentation (contributing to database of Raman spectra for planetary applications and several journal publications);
- (ix) A study of Carotenoids recovered from Eilat;
- (x) An in depth study of the capability of Raman instruments to detect reduced carbon and infer thermal maturity properties;
- (xi) Optimisation of the ExoMars RLS instrument performance (EQM) following performance modelling with the simulator;
- (xii) Presentations on the modelling and instrument development at several international conferences;
- (xiii) A field campaign in Utah as part of the UK MURFI project (during which prototype instrumentation was tested);
- (xiv) A field campaign in Boulby mine (UK) as part of the MINAR programme (during which prototype instrumentation was tested).

This work has resulted in co-authorship of 4 journal papers and 8 conference publications.

1

INTRODUCTION

We are explorers.

The common thread that ties together every living organism on this planet is the conscious (or even unconscious) desire to explore. Even in its simplest form, life searches the world around it, seeking new spaces to accommodate and grow into, pursuing fresh resources and discovering new dangers, allowing it to learn, understand and adapt to the universe it lives in. The desire to explore is primordial and fundamental to our existence. In the very short time we have inhabited this planet, we have scaled the highest mountains, plunged into the depths of the oceans and journeyed across arctic planes to the top and bottom of the Earth. With each expedition, we surpass the limits of previous missions. Our advances in science and technology have allowed us to walk upon the Moon, witness exploding stars and has unearthed hundreds of other worlds within the Universe. We have photographed the dusty Martian terrain, caught a glimpse of the harsh Venusian landscape and rendezvoused with a passing comet. The knowledge and understanding of our place in the universe that has resulted from these exploration campaigns has inspired scientists to explore even further and deeper into the unknown worlds around us. The urge to explore goes beyond our society's economic gain or technology advancements (although they are a powerful and necessary result) and allows us to address fundamental questions about ourselves, the universe and our place within it.

Space exploration, like any other expedition, brings with it many new dangers and challenges. Despite the continuous presence of humans in space (via the International Space Station, for example) the long term physiological effects of microgravity on the human body are still unknown (Wang *et al.*, 2011). Outside of the atmosphere, the human

body is exposed to a harsh radiation environment, the effects of which can severely impact human health (Schimmerling, 1992). Vital requirements such as oxygen, water and food increase mission payload envelopes and costs (potentially making manned missions a high risk operation). Until we are able to overcome these challenges, we must rely on unmanned missions that utilise satellites, landers or rovers, equipped with sophisticated analytical instruments in order to investigate and explore the solar system remotely.

These unmanned missions and the development of the analytical instruments on-board are not without their own challenges or complexities. As each new mission is proposed, the scientific goals become more and more ambitious and wide ranging (Hall and C., 1977). The technical requirements become ever more difficult to achieve. Significant advances in the miniaturisation of robust technologies are necessary to overcome the strict mass, volume and power constraints. Requirements on autonomy, memory and processing power are becoming more demanding, while instrument and spacecraft designs need to become more reliable in order to survive the longer mission lifetimes. If we are to continue revealing the secrets of the solar system, we must recognise and understand the full range of complicated trade-offs that are encountered when developing analytical instruments for space exploration.

This chapter considers key technological developments related to the recent robotic (lander and rover) exploration of the solar system and identifies the likely scientific goals and destinations of the next generation of rover and lander missions. In particular, the chapter provides a review of the Raman spectroscopy technique and the role it is likely to play in future planetary exploration missions, especially in stand-off configurations; a technique that will help to improve the efficiency and analytical capabilities of future planetary rovers.

1.1 HISTORY OF ROBOTIC EXPLORATION

1.1.1 THE MOON

Earth's only natural satellite, the Moon, resides in a tidally locked orbit at a distance of 370,300 km. The Moon carries a tenuous atmosphere mainly composed of noble gases such as Helium, neon and argon (Sridharan *et al.*, 2010), while the powdery lunar regolith

consists mainly of pulverised (from early meteor bombardment) silicate minerals (Heiken, Vaniman and French, 1991). In its soil, the Moon preserves a record of early geological evolution of the inner planets; a record lost on the more dynamic planets in the solar system (Crawford and Joy, 2014). The thin, inactive atmosphere means the surface incorporates details of the Solar wind and inner solar system activity. Further exploration of the moon will also continue to enhance human understanding of the origin of the Earth-Moon system as well as that of the solar system. Through exploration, the moon becomes a platform for advancements in astronomy, medicine and astrobiology (Cockell, 2010). Continued study of the moon is also the initial step in establishing the moon as an exploration base and a launch pad for voyaging to bodies further out into the solar system, such as Mars and satellites of the gas giants (Crawford and Joy, 2014 and Cockell, 2010).

In 1959, Luna 2 (a Soviet lead mission) was the first spacecraft to reach the surface of another celestial body (see illustration of the lander in Figure 1.1). The craft successfully impacted on the surface of the Moon, carrying instruments such as magnetometers, that relayed data during the descent to the lunar surface (Ulivi and Harland, 2007).

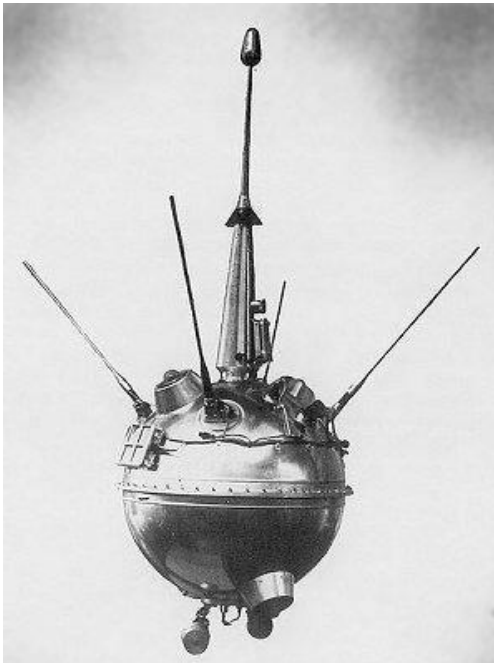


Figure 1.1: A concept image of the Luna 2 spacecraft lead by the Soviet Union. Credit: NASA

Shortly thereafter, the United States developed its own Lunar Exploration Program, first with the launch of Ranger 4, an impactor destined for the far side of the moon (see Figure 1.2). This was followed by Ranger 6, 7, 8 and 9, each of which successfully imaged separate areas of the lunar surface and deployed impactors (Kosofsky and El-Baz, 1970).

Following this, the United States launched the Surveyor Program in preparation for the Apollo Program. The Surveyor Program successfully deployed 5 landers on the surface of the Moon, demonstrating a soft landing at potential Apollo landing sites. Each payload consisted of several camera systems, thermal sensors and an Alpha-Particle instrument which aimed to characterise the thermal, mechanical, geochemical and magnetic properties of the lunar soil (Turkevich, Franzgrote and Patterson, 1967).

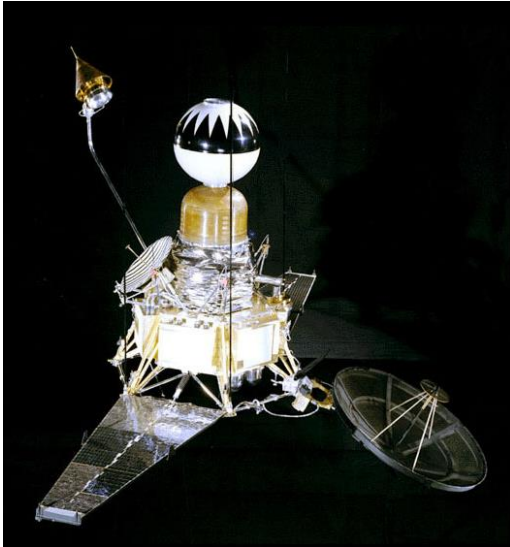


Figure 1.2: A high-resolution image of the Ranger 4 craft developed as part of the Lunar Exploration Program. Credit: JPL

Between 1961 and 1975, 12 successful Apollo missions put a total of 12 humans on the Moon and returned 381.7 kg of lunar rock (Heiken, Vaniman and French, 1991). In parallel, the Soviet Union programme continued through the series of Luna missions. Luna 16, 20 and 24 returned a total of 0.32 kilogrammes worth of samples obtained from various locations giving a wider picture of lunar mineralogy (Heiken, Vaniman and French, 1991). Additionally, Luna 12 measured the composition of the surface using X-Ray Fluorescence (XRF) and performed a surface radiation assessment (Mandel'Shtam *et al.*, 1968).

Lunar exploration activity slowed thereafter until 1994 when the National Aeronautics and Space Administration (NASA) launched the Clementine missions with the aim of mapping the lunar surface (Nozette *et al.*, 1994). NASA subsequently launched the Lunar Prospector orbiter/impactor in 1999 (see Figure 1.3 and Figure 1.4). The impactor was jettisoned into a crater located by the southern pole, with the aim of looking for evidence of ice water (Binder, 1998).

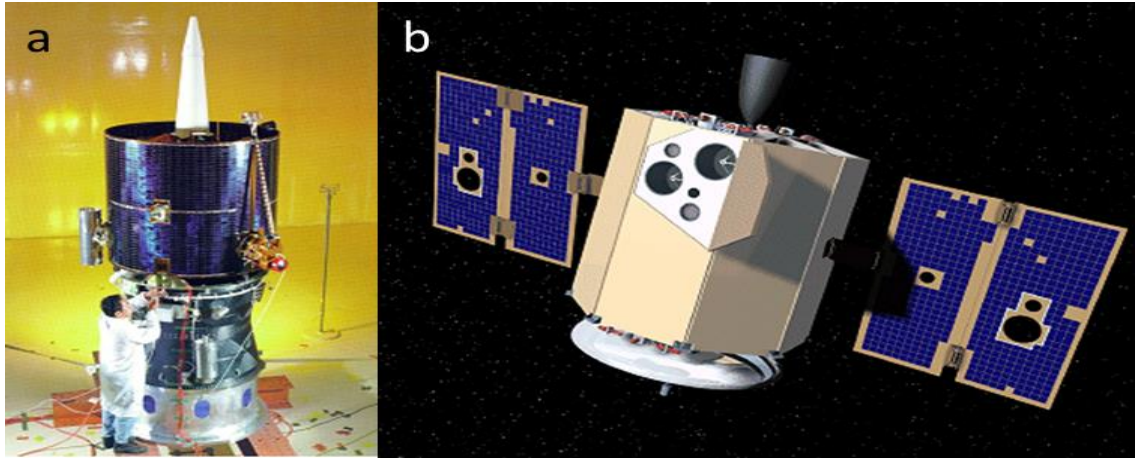


Figure 1.3: (a) The photograph of the assembly of the Lunar Prospector spacecraft. Credit: NASA. (b) An artist's impression of the Clementine Spacecraft. Credit: NASA

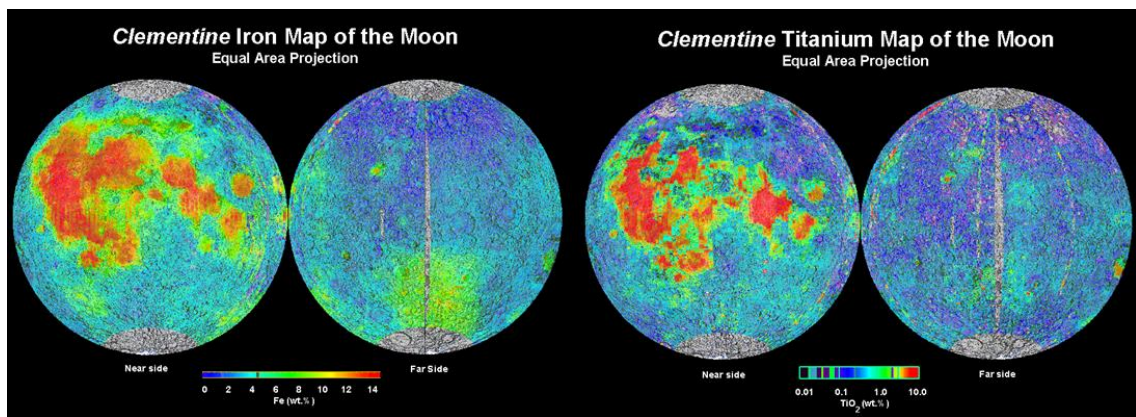


Figure 1.4: A map portraying data from the Clementine mission, showing the iron (observed at 750 and 950 nm) and titanium (observed at 415 and 750nm) concentrations in the lunar soil. Credit: Lucey et al. 2000.

In 2003, SMART-1 was launched, the European Space Agency's (ESA) first lunar mission (see Figure 1.5). The SMART-1 orbiter performed the first global X-ray and infrared spectral mapping of potential resources (such as magnesium, aluminium and silicon) and mineralogy at a 50 km resolution (Foing *et al.*, 2003).

In the same year, the Chinese National Space Administration (CNSA) initiated the Chinese Lunar Exploration Program (CLEP). The on-going programme, features 3 phases; orbiting the moon, landing on the surface and then returning (Zheng *et al.*, 2008). In 2007, the CNSA launched Chang'e-1, shortly followed by Chang'e-2 in 2010. These reconnaissance missions paved the way for Chang'e-3; the second phase of CLEP. Chang'e-3 encompassed a lander and a rover equipped with remote sensing instrumentation such as a stereoscopic camera, an Alpha Particle X-ray Spectrometer

(APXS), a Visible- Near Infra-Red spectrometer and, for the first time, a ground penetrating radar (Ip *et al.*, 2014).



Figure 1.5: ESA's Smart-1 spacecraft being positioned upon Ariane 5's central cryogenic stage. Credit: ESA

Many of the previous missions to the moon, many of which are orbiters, have focused on mapping potential resource in preparation for future human exploration. The use of Raman spectroscopy (a molecular identification technique described in detail in Section 1.3) would provide in situ verification of past orbital measurements. The technique, which has been recently considered by Carpenter *et al* (2010) for a future moon mission, would offer new information on mineralogical composition and structure (which would allow for material classification) of surface regolith and give insight into the landing site's water environment.

1.1.2 MARS

Mars is a cold and desolate planet. The surface regolith is composed mainly of iron oxide, a highly oxidising material, while the thin (600 Pa) atmosphere is mostly composed of carbon dioxide. The surface temperature of Mars ranges from 180 K to 230 K (Barlow, 2008). However, current climate models and observed surface geology suggest that Mars had a warmer and wetter past (Squyres and Kasting, 1994) making it a potential habitat for life (Cockell and Raven, 2004). Models also suggest that the smaller mass of Mars (compared to that of Earth), erosion and volatile deposition into the crust, resulted in a

loss of atmosphere (and therefore the climate we see today) (Ellery *et al.*, 2004). The thin atmosphere (and lack of internal magnetic field) also results in a hazardous radiation environment. The surface of Mars is bathed in ultra-violet radiation, penetrating the soil up to 2 mm (Cockell *et al.*, 2000). If life exists or ever did exist on Mars, it would have most likely inhabited the sub surface away from the harsh surface environment (Cockell *et al.*, 2000). Mars's potentially warm and wet history make Mars a key target for finding evidence of extinct or extant life elsewhere in the solar system.

In 1976, NASA became the first agency to successfully land a spacecraft on the surface of Mars. The Viking mission consisted of two identical orbiter-lander craft; Viking 1 and Viking 2 (see Figure 1.6). Both craft were launched in 1975 and reached separate destinations on the surface of Mars in 1976. The mission aimed to assess the geology, temperature and weather profiles of the landing sites and to look for signs of microorganisms. The lander payload included an infra-red spectrometer, a Gas Chromatograph Mass Spectrometer (GCMS) and an XRF instrument (Soffen, 1977). The landers also contained a suite of biology experiments, the results of which are still a source of debate (Thomson and Schultz, 2007).

The next craft to reach the surface of Mars was Pathfinder, launched by NASA in 1996. The mission was a cost effective, technology demonstrator that aimed to determine if the rocks in the region of the landing site were of volcanic origin (Golombek *et al.* 1997). Pathfinder was the first lander on Mars to deploy and navigate a rover (named Sojourner), which was equipped with three science and ten technology experiments, including an imager, an atmospheric/meteorological science package and an Alpha Particle X-ray Spectrometer (APXS) instrument (Golombek *et al.* 1997).

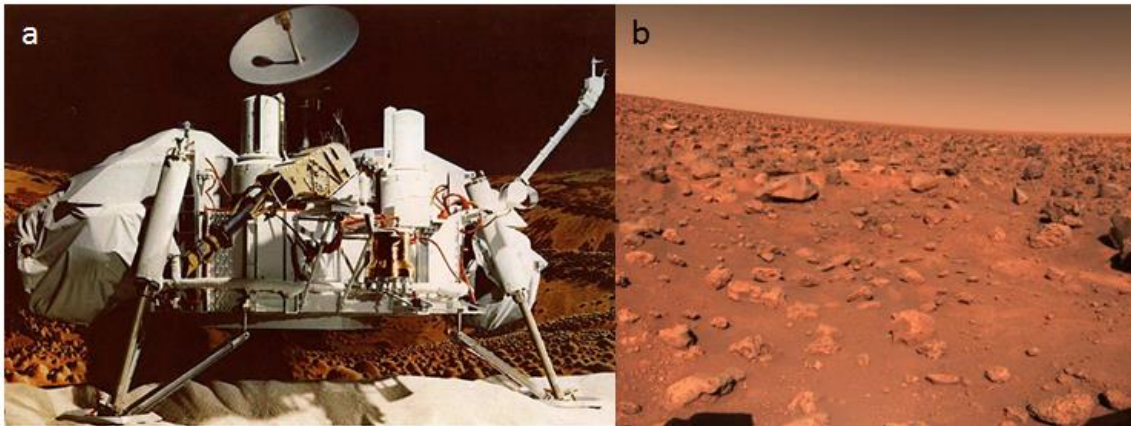


Figure 1.6: a) An image of the Viking Lander. Credit: NASA. b) An image acquired by Viking 2 of the landing site. Credit: JPL.

In 2003, ESA launched Mars Express, its first mission to another planet, which incorporated both an orbiter, and a lander named Beagle 2 (Figure 1.7). The mission had a very short development phase (5 years from concept to launch), resulting in a cost effective programme compared to other Mars missions (Chicarro, Martin and Trautner, 2004). The Beagle lander included a panoramic, stereoscopic camera system and a sample collection system. Other instruments included a microscope, a Mossbauer spectrometer and an XRF spectrometer. The payload also included a gas analysis and organic chemistry package. The mission aims were to investigate the geology, mineralogy and chemical composition of the landing site, in addition to looking for life signatures (Wright, Sims and Pillinger, 2003). Unfortunately, contact with the lander was lost upon entry, during the descent towards the chosen landing site, Isidis Planitia (Bridges *et al.*, 2003).



Figure 1.7: An artist's impression of the Beagle 2 lander. Credit: ESA

In the same year, NASA launched the Mars Exploration Rover (MER) programme, which consisted of two identical rovers (Figure 1.8(a) and (b)). The primary mission goal was to search for evidence of subsurface water through observable chemical and geological interactions i.e. clays, salts and carbonates that form in the presence of water. Other mission goals included characterising the climate and geology of the landing site (see 8(c)) and assessing the environmental conditions for future human exploration (Crisp *et al.*, 2003). The payload for the rovers (nicknamed Spirit and Opportunity) included a mast mounted panoramic camera system (Figure 1.8(d)), a thermal emission spectrometer and a microscope imager. Other instruments included a Mossbauer spectrometer and an APXS instrument (Arvidson *et al.*, 2010). Both rovers outlasted their original designed lifetimes (90 days); Spirit continued to operate for 6 years in total, while Opportunity continues to explore the surface of Mars today. Early on in its mission, Opportunity has detected materials such as hematite and jarosite, minerals that generally form in the presence of water and acidic water respectively (Klingelhöfer *et al.*, 2004). The images of the surfaces obtained using the panoramic camera system show the presence of crossbeds (Figure 1.8(c) for example). Crossbeds are geological features that indicate past water flow (Parker, Haldemann and Team, 2005) .

Following on from the successful deployment of Spirit and Opportunity, NASA's Mars Exploration programme launched the Phoenix lander mission (1.9(a)). The craft reached the surface in the northern polar regions of Mars in 2008 with the objective of assessing

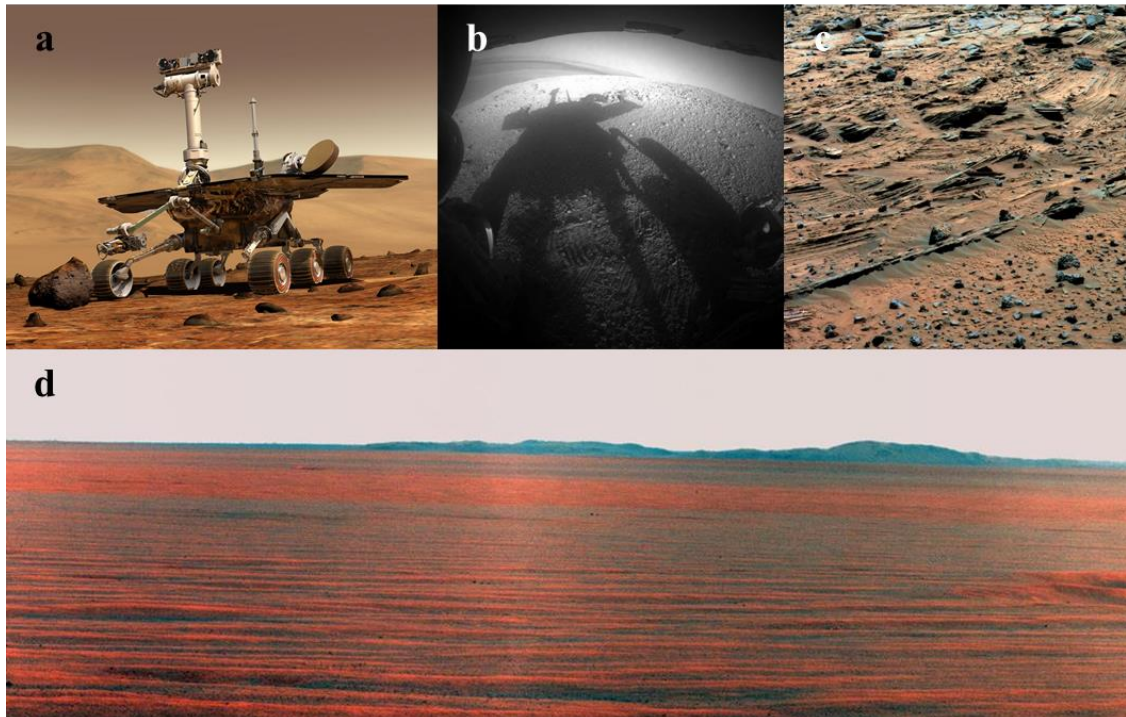


Figure 1.8: A compilation of images from NASA's Mars Exploration Rover Mission. Image (a) is an artist's impression of a Mars Exploration Rover. (b) An image taken by Opportunity of its own shadow at the craft landing site. (c) An image taken by the Spirit rover of the layering pattern observed in the soil close to the landing site and (d) is a panoramic image taken by the Opportunity Rover on the rim of the Endeavour Crater. Credit: NASA

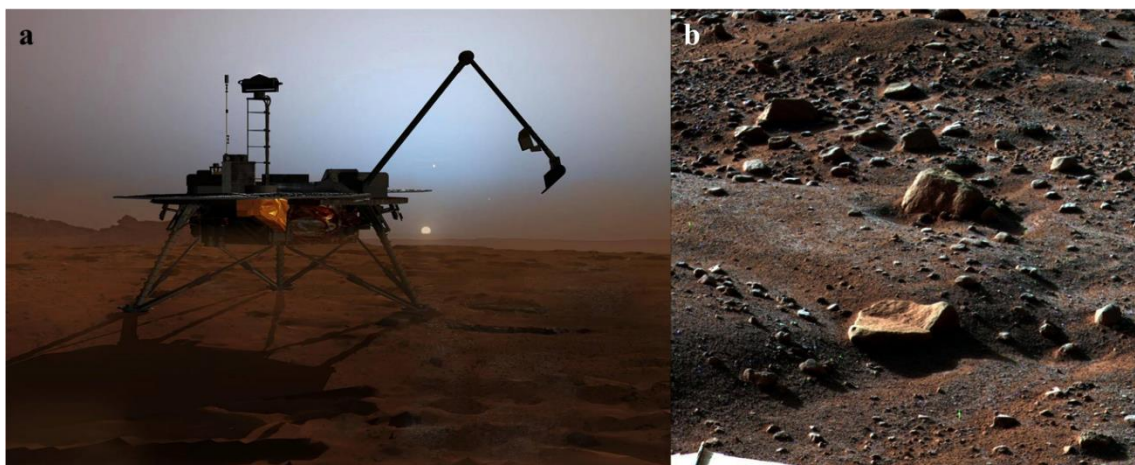


Figure 1.9: (a) shows an artist's impression of NASA's Phoenix Lander shutting down operation as the Martian Winter brings periods of very little sunlight. (b) An image taken by the Stereo Imager on board the Phoenix Lander. The image shows a thin layer of water frost on the nearby surface. Credit: NASA

the habitability of the polar ice-soil and climate. The lander included a wet chemistry laboratory, an atomic force microscope and thermal and electrical conductivity probes (Kounaves *et al.*, 2010). During its 5 month long mission, the lander found H₂O frost on the surface of the planet (see Figure 1.9(b)) and successfully measured the interaction between ice and vapour with aqueous minerals (such as CaCO₃) in the Martian soil (Smith *et al.*, 2009).

After the success of the MER mission and the Phoenix lander, NASA launched the Mars Science Laboratory (Figure 10(a)). Nicknamed Curiosity, the rover is the largest craft to reach the surface of Mars and continues to operate beyond its expected lifetime of 23 months. The rover landed in the Gale crater in 2012 with the intention of assessing the past and present day habitability on Mars. Equipped with an array of scientific instrumentation, the rover aims to analyse the geological and mineralogical history of the Gale crater. The integrated GCMS and gas analyser package are designed to detect organic carbon in the soil and atmosphere, while the X-ray diffractometer aims to determine the diversity of minerals at the landing site. The on-board APXS and neutron spectrometer provide information on soil chemistry and water content of rocks

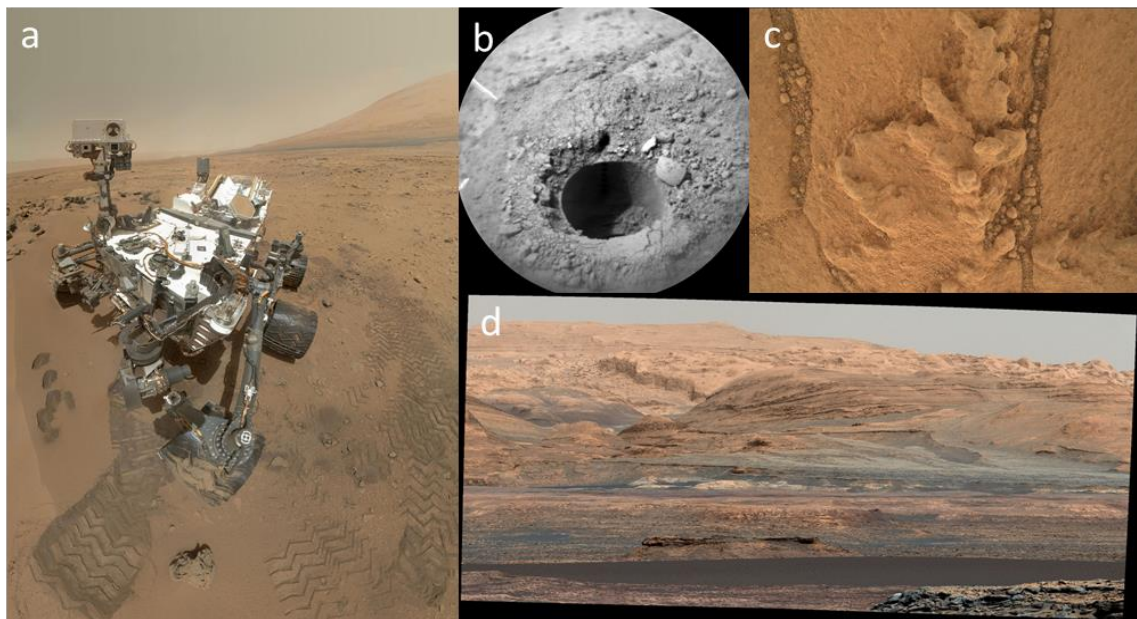


Figure 1.10: Image (a) shows a ‘self portrait’ of the Curiosity Rover taken using the on-board arm-mounted camera. (b) shows an image acquired by the MArS Hand Lens Imager (MAHLI) of one of the holes drilled into the base of Mount Sharp. Image (c) was also acquired by MAHLI and shows a close up view of erosion-resistant materials. Similar features are found on Earth and form when shallow bodies of water begin to evaporate and minerals precipitate from concentrated brines. Image (d) shows the landscape as seen by Curiosity’s MastCam instrument at the base of Mount Sharp. Credit: NASA

respectively. The focusable mast mounted camera system provides colour images of the surrounding landscape (see Figure 1.10(d)) and regolith. This is coupled with the Laser Induced Breakdown Spectrometer (LIBS) measurements which provides information on the regolith composition on small sample areas (an example is given by Figure 1.10(c)) (Grotzinger *et al.*, 2012). The rover also features a Sample Acquisition, Sample Processing, and Handling (SA/SPaH) subsystem. The SA/SPaH acquires rock and soil samples from the surface of the planet (Figure 1.10(b) shows a hole drilled by the SA/SPaH), processes them into fine particles and distributes them to the analytical science instruments and scientific analysis.

Since it's delivery to Mars, the Curiosity rover has measured hydrogen, oxygen, sulphur, nitrogen, and phosphorus within the Martian soil as well as identifying organic carbon preserved in the mudstone (Freissinet *et al.*, 2015). Curiosity has also detected methane in the Martian atmosphere, the sources of which are still unclear (Webster *et al.*, 2015).

1.1.3 VENUS

Venus is often referred to as Earth's sister planet due to their remarkably similar mass and size. With the planet also residing at a relatively similar solar distance (compared to Earth), Venus has been the target of numerous exploration missions over the last 40 years. Observations and planetary models suggest that Venus and Earth formed in close proximity with their atmospheres comprising of similar gasses (Chassefi Ere *et al.*, 2012). However, the Venusian atmosphere is an example of a "runaway greenhouse effect" (Kasting, 1988). As a consequence of its proximity to the sun and thick atmosphere, the additional heat became trapped, increasing the global temperature. The present day surface temperature is around 730 K, with an atmospheric pressure of 91 bar (Bullock, 2001). The atmosphere is mainly composed of CO₂ with a global cloud deck of H₂SO₄ (Crisp *et al.*, 2002); it is this cloud deck that prevents observation of the Venusian surface at visible wavelengths (Crisp, 1986). However, orbiters using radar and surface landers have revolutionised our knowledge of Venus as they have been able to probe beneath the thick reflecting atmosphere.

In 1970, Venera 7, a Soviet Union lander, became the first lander to reach the surface of Venus (Figure 1.11(a)). However, the mission was only partially successful as only the temperature and pressure monitors worked once on the surface (Basilevsky *et al.*, 2007). Measurements taken by Venera 7 were later confirmed by its sister craft, Venera 8, shown in Figure 1.11(b). Venera 8 was able to take photometric measurements and assess the level of sun light reaching the surface of Venus (a sunlight level similar to Earth on an overcast day). Both Venera 7 and 8 contained gas analysers and gamma ray spectrometers, which were used to analyse the potassium, thorium and uranium ratios in the soil (Basilevsky *et al.*, 2007).

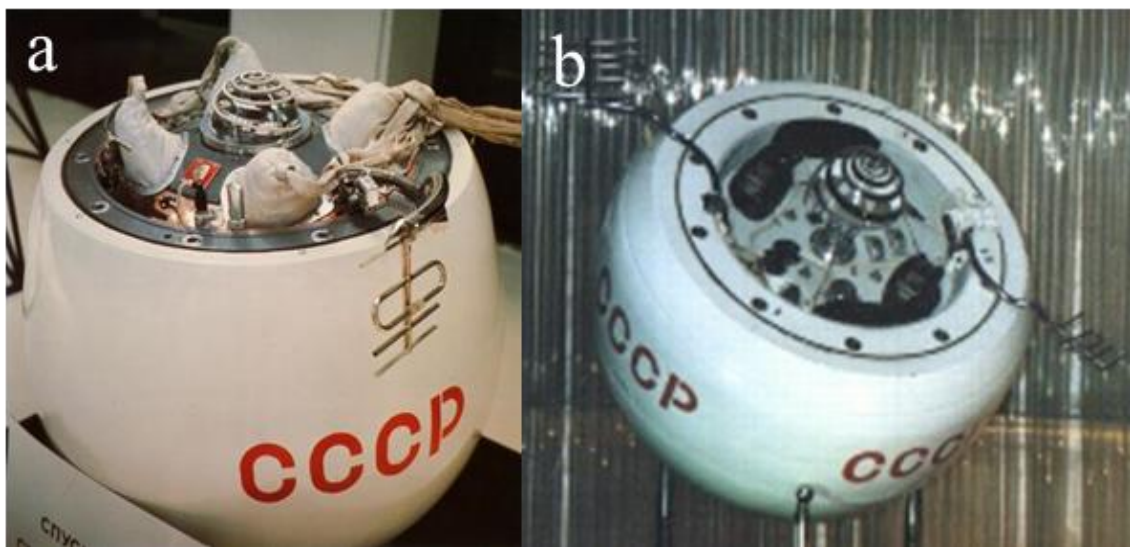


Figure 1.11: Images of the Venera 7 (a) and Venera 8 (b) landers launched by the Soviet Union in 1970. Credit: NASA

Five years later Venera 9 and 10 were launched and landed at two separate locations on the surface of Venus. The craft were based on the Venera 8 architecture, and also contained a gamma ray spectrometer. Venera craft 9 and 10 also contained stereoscopic cameras which obtained first (panoramic) images of the surface of Venus (see Figure 1.12) (Keldysh, 1977). The images showed areas of both soil and finely bedded rock. Similarly, Venera 11 and 12 reached the surface of Venus in 1978 at two additional locations on Venus. However, they were unable to acquire surfaces images due to a fault in the camera system (Basilevsky *et al.*, 2007).

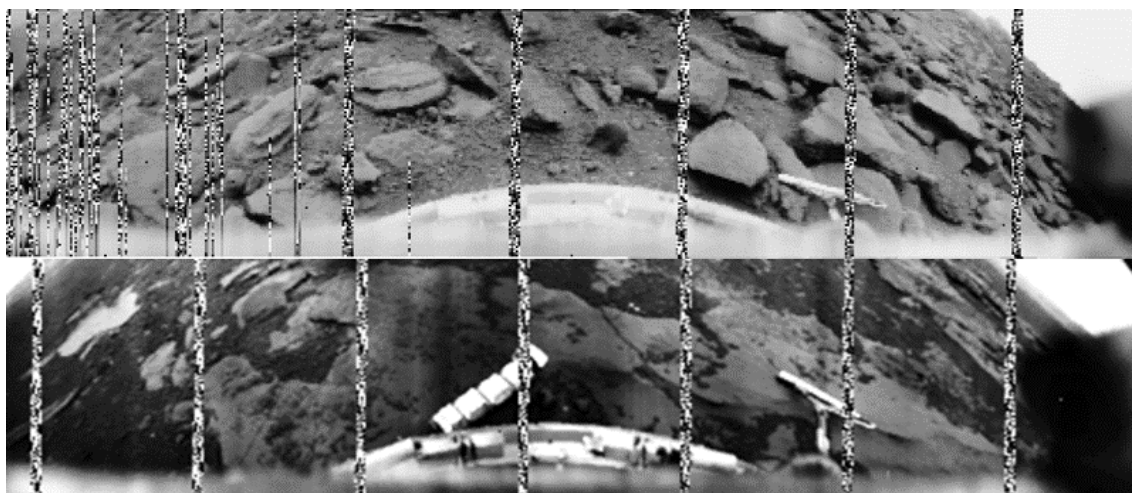


Figure 1.12: Images by the stereoscopic cameras on board the Venera 9 (top) and Venera 10 (bottom) spacecraft's. Credit: NASA Goddard Space Flight Center

The designs for Venera 13 and 14 were significantly more advanced compared to the previous craft (Florensky *et al.*, 1983). Venera 13 and 14 were able to pull samples into a capsule from under the lander in order to be analysed by XRF and gamma ray spectrometers that were utilised to identify various mineral such as SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CrO and K_2O likely to reside in basaltic rocks. The XRF and GRS data that were obtained have led to various comparison studies with terrestrial analogues to help infer the geology of the Venusian material (Basilevsky *et al.* 1985; Basilevsky *et al.* 2007).

Due to the extreme surface temperature and atmospheric pressure, the Venera missions were short-lived; surface operation times ranged from 23 (Venera 7) to 127 minutes (Venera 13). Equally, subsequent missions such as Vega 1 and 2, which were launched in December 1984, survived on the surface for 20 and 56 minutes respectively (Esposito, Stofan and Cravens, 2007). The landers were based on the Venera 9 architecture and both included XRF spectrometers. The rock morphologies indicated by the Vega probes suggest that the landing site material was formed by erupting fluid lavas (Head *et al.*, 1992).

Despite the success of the Venera missions, this section has highlighted that the information gained from the missions has been limited to that provided by XRF instrumentation, i.e. elemental composition of the surrounding surface material. Although much can be inferred from this technique, the incorporation of an instrument that provides molecular information on a future mission would provide key mineralogical

confirmation. Techniques such as Raman spectroscopy are capable of providing information on mineral phases and structure which aid our understanding of surface geology and atmospheric composition (Wang, 2009). The use of Raman spectroscopy instrumentation for Venus exploration is discussed further in Section 1.3.4 of this Chapter.

1.1.4 EUROPA

Despite never having been the target of a lander or rover mission, Europa has become one of the major extraterrestrial objects of interest in the field of astrobiology and is therefore a potential target for a number of different proposed future lander missions (see Section 1.2.4). Various fly-by missions, including NASA's Voyager 1 and the Galileo spacecraft (Anderson *et al.*, 1998) and several astronomical observations, such as those conducted by the Hubble Space Telescope, have shown that Europa (one of the Galilean moons of Jupiter), is a cold and ice covered world (Carr *et al.*, 1998; Kargel, 2000). Figure 1.13 shows an image of the surface of Europa that was acquired by Voyager 1 during a Jovian fly-by. Although the moon receives a very small amount of solar energy, theoretical heat transfer models and geological features present on the icy surface suggest the presence of a sub-surface ocean (likely maintained by tidal forces from Jupiter), making it a potential habitat for extreme life (Chyba and Phillips, 2002) (Raulin, 2005).

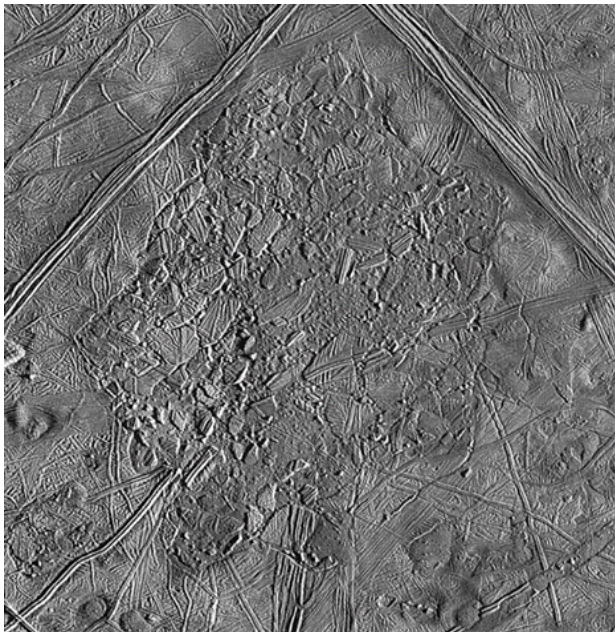


Figure 1.13: An image of the surface of Europa taken by the Voyager 1 spacecraft during a fly-by of the moon. The image depicts a 200km area of the icy surface. The ridges and marks on the ice surface are evidence of recent geological disruption and the presence of newer material (compared with its surroundings) on the surface. These surface features may be the product of a sub-surface liquid layer. Image taken from Figure 1. in (Carr *et al.*, 1998).

In terms of future exploration, much could be gained by deploying an instrument such as a Raman spectrometer onto the surface of Europa. Raman spectroscopy provides molecular information of target material and will therefore enhance our understanding of the surface materials and its molecular content. Many studies have also demonstrated the techniques ability to detect bio-signatures and water within host material (Jorge Villar and Edwards, 2004; Fernando Rull *et al.*, 2011). The potential of Raman spectroscopy for Europa exploration is discussed in Section 1.3.4.

1.1.5 TITAN

Titan is the largest moon of Saturn and the second largest moon in the solar system. In 1980, observations by the Voyager probe during a brief fly-by, suggested that Titan's thick nitrogen atmosphere is rich in organic compounds and methane (Hanel *et al.*, 1981). Results of the infra-red investigations have suggested that continuous chemical reactions, along with the generation of complex organics, meaning that Titan could be an example of the pre-biotic chemistry, similar to that of a primitive Earth (Raulin *et al.*, 2012).

In 1997, Cassini-Huygens (a NASA/ESA collaborative mission) was launched, towards the Saturnian system. The mission encompassed a NASA developed orbiter (Cassini) and an ESA built Titan lander (Huygens). Once on the surface of Titan, the probe was able to image the surrounding area (see Figure 1.4(b)) and identified a possible energy source for atmospheric chemistry in addition to obtaining information about the atmospheric composition and structure (Niemann *et al.*, 2010). The probe aimed to analyse surface geology and infer internal structure properties. It also had the ability to study aerosol

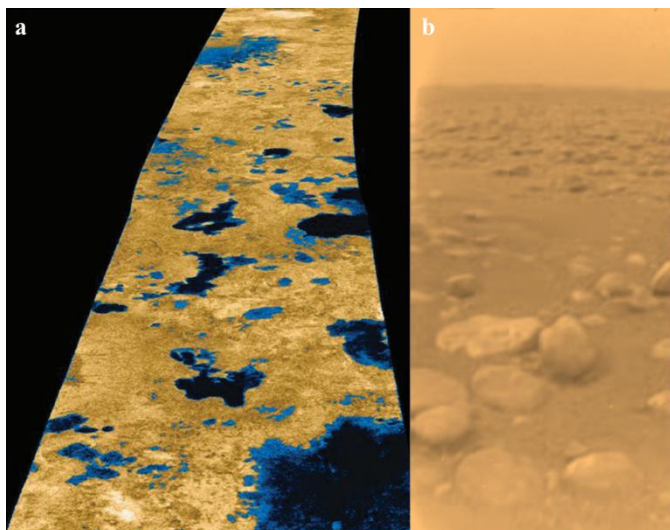


Figure 1.14: Panel (a) shows a Radar image (acquired by the Cassini Spacecraft) of surface Lakes and seas in northern region of Titan. Image (b) was acquired by ESA Huygens DISR camera and shows the first view of Titan's surface (Credit: NASA/JPL/USGS).

properties and measure global temperatures and wind speeds (Lebreton *et al.*, 2005). The Huygens payload includes a descent imager, aerosol analyser, GCMS and surface science package (Matson, Spilker and Lebreton, 2002).

In terms of the future exploration of Titan, techniques such as Raman spectroscopy could provide information on the presence and abundance of organic material and complex molecules such as biomarkers and protein-like molecules (Sobron *et al.*, 2014). Section 1.3.4 discusses the potential use of Raman spectroscopy for Titan exploration.

1.2 FUTURE ROBOTIC MISSIONS

1.2.1 THE MOON

In recent years, scientific interest in lunar exploration has increased significantly. Studies have highlighted that there are still many unknowns surrounding the origin of the Earth-Moon system and the distribution of minerals and water within it. The moon is also a possible candidate for In Situ Resource Utilisation (ISRU). ISRU is the process of producing raw materials from the lunar regolith and crust (Landis, 2007). In addition, Cockell et al. (2010) suggested that the moon could be utilised as a ‘stepping-stone’ for rapid and easy exploration of the rest of the solar system. In light of this, various space agencies and private sector companies are making plans to return to the moon.

ESA is currently developing the European Lunar Lander, originally proposed to launch in 2018 (see Figure 1.15). The mission will act as a precursor to future lunar missions, demonstrating a soft landing within a predetermined landing site in the south polar regions (Carpenter *et al.*, 2012). Amongst many other science goals, the lander and rover will begin to assess the availability, distribution and abundance of potential ISRU. In order to facilitate human exploration in the future, the mission will aim to identify and assess high priority resources such as oxygen, H₂O and silicon, which play a key role in fuel manufacture as well as human habitability (Landis, 2007). While the final scientific payload is still under consideration, analytical instruments such as a Raman spectrometer, panoramic cameras, a LIBS spectrometer, mass spectrometer, electron and ion spectrometer, optical microscope and atomic force microscope, have been identified as potential instruments to fulfil the pre-determined science requirements (Carpenter *et al.*, 2012; Coates *et al.*, 2012).

Following on from the success of Chang'E- 1, 2 and 3, the CNSA will continue the Chang'E project into its final phase with the launch of a lunar rover mission (Chang'E-4) and a sample return mission (Chang'E-5) in 2017 (Lin and Ziyuan, 2014). Chang'E-4 will demonstrate a soft landing and lunar vehicle technique, acquire geological in situ measurements of the lunar surface and map the Earth's plasmasphere (Lin and Ziyuan, 2014).



Figure 1.15: An artist's impression of ESA's first Lunar Lander. The lander will demonstrate key technologies in the lead up to future human exploration of the Moon. Credit: ESA

In 2018, India are planning to launch India Chandrayaan-2, an orbiter and rover mission. The Chandrayaan-2 orbiter will include an X-ray spectrometer (Narendranath *et al.*, 2014), a RADAR system capable of detecting ice water a few tens of metres below the lunar surface, an IR spectrometer to provide a wide wavelength study of surface minerals and a neutral mass spectrometer to interrogate the lunar exosphere. The orbiter will also include a Terrain Mapping Camera that will provide three dimensional maps of surface geology and minerology (Mylswamy *et al.*, 2012). The rover will include an APXS instrument and LIBS instrument to allow in situ measurements of surface composition (Mylswamy *et al.*, 2012; Shanmugam *et al.*, 2012).

As part of the Deep Space Gateway, NASA are developing the concept of placing a manned vehicle at the L2 (Lagrange) point of the Earth-Moon system which resides beyond the far side of the moon. The mission will serve as a demonstration of advanced life support and communication technology for longer deep space manned missions, to Mars for example (Burns *et al.*, 2013).

1.2.2 MARS

In 2001, ESA initiated the Aurora programme, a long-term plan to develop the technology and expertise to facilitate robotic, and eventually human, exploration of Mars and other solar system bodies (Baglioni *et al.*, 2006). The first flagship mission of the ongoing Aurora programme is ExoMars, a joint ESA and Russian Federal Space Agency (Roscosmos) exploration and astrobiology programme. ExoMars consists of two separate missions, the first of which is an orbiter mission that successfully launched in January 2016. The orbiter includes a trace gas analyser developed to investigate the Martian atmosphere, and an Entry, Descent and Landing Demonstrator Module (EDM) (Vago *et*

al., 2015). The EDM descended into the Martian atmosphere in October 2016 in order to demonstrate an ability to deliver a payload to the Martian surface. However, contact with the module was lost shortly before touchdown (Blancquaert, 2016). The second mission, scheduled for launch in 2020, consists of the ExoMars rover. Unlike previous rovers, ExoMars is equipped with a drill capable of retrieving soil samples from 2m below the Martian surface (Vago *et al.*, 2015). The samples are then passed to an analytical drawer of instruments (via a sample delivery system), designed to characterize the geochemistry and water environment of the Martian surface and subsurface to search for signs of extant or extinct life. The rover payload includes a Panoramic Camera (PanCam) that will obtain context images from a distance of up to one kilometre (Coates *et al.*, 2015), coupled with a long range infrared spectrometer (ISEM). The mast mounted system will remotely provide structural, textural and compositional information on the surrounding Martian soil (Korablev *et al.*, 2014). The rover also contains a close-up imager (CLUPI) capable of acquiring high-resolution colour images of rocks, soils, drill fines and core samples (Josset *et al.*, 2012) and a ground penetrating radar (WISDOM) to characterise the subsurface stratigraphy and water content in addition to providing context for the subsurface drill samples (Ciarletti *et al.*, 2015). Integrated into the drill is an IR spectrometer (Ma_Miss) that will determine soil characterisation and mineralogy within the drill borehole (De Sanctis *et al.*, 2014). Once crushed, the excavated samples are delivered to an analytical laboratory consisting of a visual and infrared imaging spectrometer (MicrOmega) (Pilorget, Bibring and Team, 2012) and a Mars Organic Molecule Analyser (MOMA) which is composed of a Laser Desorption Mass Spectrometer (LDMS) and a GCMS system (Buch *et al.*, 2015). The science payload also contains a Raman Laser Spectrometer (RLS), a novel instrument that has never before been utilised for space exploration (Moral *et al.*, 2016) (see Section 1.3.4 for a detailed description of RLS).

NASA's next mission to Mars is also due for launch in 2020. The mission will assess the past and present habitability and geological history of the landing site; assess bio-signature preservation given present Martian conditions (Mustard *et al.*, 2013). The mission will also serve as a demonstration of new techniques by implementing a sample cache for the first time. The rover will contain seven science instruments (see Figure 1.16); MastCam-z, a stereoscopic imaging system that will be used for rover operations and context imager for mineralogical investigations (Bell III *et al.*, 2016); an XRF

instrument that will provide elemental composition of the Martian soil (PIXL) (Allwood, Wade and Hurowitz, 2015). MOXIE is an In Situ Resource Utilisation (ISRU) experiment that will investigate the process by which oxygen can be retrieved from the Martian atmosphere (Hecht and Hoffman, 2016). Finally, the rover contains a meteorological science package that will measure temperature, wind speed and direction, pressure and landing site humidity. The instrument will also characterise dust size and morphology and will investigate how lifted dust impacts the local weather and climate (Rodriguez-Manfredi *et al.*, 2016). The rover also encompasses two Raman spectrometers: SuperCam and the Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC) instrument, which are discussed in detail in Section 1.3.4.

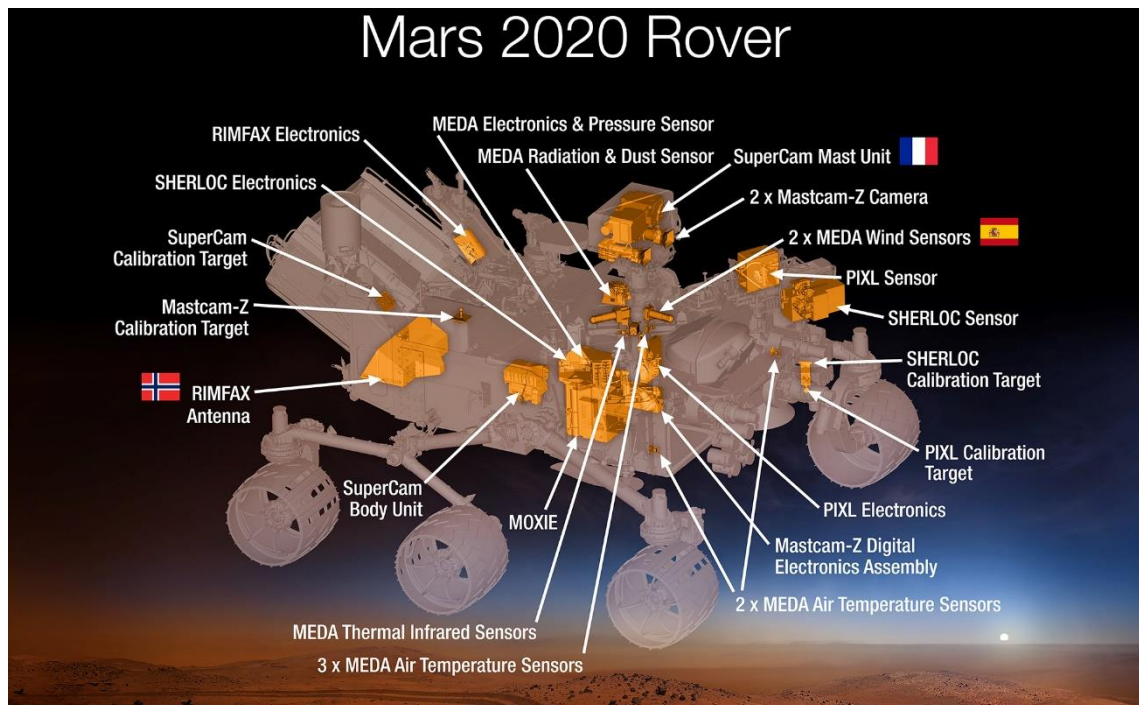


Figure 1.16: A schematic of NASA's Mars2020 rover. The diagram highlights the main instrument subsystems. Credit: NASA

1.2.3 VENUS

In 2015, NASA's Discovery programme selected two Venus missions for further refinement and concept design studies for a future flight opportunity. NASA's Goddard Space Flight Centre proposed the Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging (DAVINCI). The instrument project will measure the chemical

composition of the Venusian atmosphere during a 63 minute descent to the planetary surface. The mission would focus on assessing the possibility of active volcanoes and would characterise the surface-atmosphere interactions (Glaze *et al.*, 2016). The second mission is a JPL led orbiter mission, VERITAS (Venus Emissivity, Radio Science, InSAR, Topography, and Spectroscopy). In the project, the orbiter would produce high-resolution images of the surface to produce composition maps and topographical information on the Venusian surface (Hensley, Smrekar and Pollard, 2012).

Recently, Wang et al (2016) proposed that a mature in situ Raman spectrometer could provide answers to several key questions still surrounding the exploration of Venus. The proposed Raman instrument would provide definitive evidence of the presence of minerals such as carbonates and silicates, confirming their stability at the surface. Raman spectroscopy is also capable of identifying traces gases in the atmosphere such as H_2SO_4 - H_2O , HSO_3 - H_2O and sulphide and sulphate materials, by products of the planet's sulphur cycle.

1.2.4 EUROPA

While in situ exploration of Europa is currently too technically challenging, NASA are developing a Europa Jupiter System Mission (EJSM); a reconnaissance orbiter mission to investigate the subsurface oceans, ice shell, surface organic and inorganic chemistry and geology (Clark *et al.*, 2011). In 2015, NASA selected the mission payload based on high technology readiness level (TRL), heritage and previous mission results. The payload will include a penetrating RADAR, a Visible-IR spectrometer, a UV spectrometer and an Ion Neutral Mass spectrometer. The payload will cover a wide range of wavelengths in order to explore the moon's surface composition, chemistry and geology. The payload will also include a magnetometer to investigate the strength and direction of the moon's magnetic field and to determine the depth and salinity of the subsurface ocean (Prockter *et al.*, 2011).

1.2.5 TITAN

Since the success of Cassini- Hygens, Titan has become a high priority target for exploration. In 2006, NASA listed Titan as a high priority target on its Solar System Exploration (SSE) Roadmap (National Aeronautics and Space Administration, 2006). Titan also became a key aspect of ESA's Cosmic Vision Program Themes in 2003 as well as a potential feature of its discovery missions (Reh, Coustenis, *et al.*, 2009). Since then, NASA and ESA have jointly proposed the Titan-Saturn System Mission (TSSM) (Coustenis *et al.*, 2009). The baseline concept for the mission includes both an orbiter (provided by NASA) and a lander (designed by ESA) which together, will investigate the surface geology, hydrology, meteorology, and aeronomy present in the system. A suggested lander payload includes GCMS instrument, a spectral imager, meteorological package, an acoustic sensor and magnetometer (Reh, Coustenis, *et al.*, 2009; Reh, Erd, *et al.*, 2009).

1.3 RAMAN SPECTROSCOPY

1.3.1 THEORY

Raman Spectroscopy is a chemical and structural identification technique based on the inelastic scattering of light by vibrating molecules. This section uses the classical descriptions given by (Lewis and Edwards, 2001; McCreery, 2005; Ferraro and Nakamoto, 2012; Smith and Dent, 2013) to outline the physics of the technique and how it differs from alternative scattering phenomena and molecular absorption processes.

The classical picture of Raman spectroscopy describes the intrinsic vibrational modes of a simple diatomic molecule within a sample. Analogous to two masses connected by a spring, the vibration of the molecular system can be described according to Equation 1.1,

$$q = q_0 \cos(2\pi\nu t) \quad 1.1$$

where, q is the total displacement of the masses within the molecule at time t , q_0 is the equilibrium displacement of the masses and ν is the molecular vibration frequency. Figure 1.17 illustrates this vibration motion of the molecule. Similar to the mass and spring analogy, ν depends on the strength of the bonds and the reduced mass of the system, both of which are fundamental properties of a material's molecules.

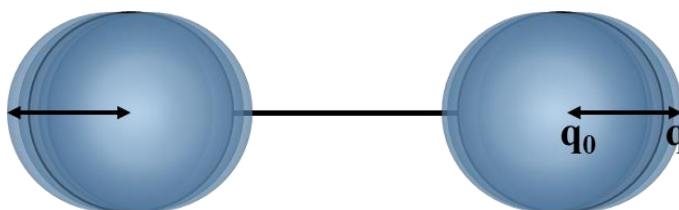


Figure 1.17: A diagram showing the intrinsic vibrational state of a diatomic atom. The total displacement of the nuclei is depicted by q , where q_0 is the equilibrium position of the masses.

Raman spectroscopy is based on the interaction of incident light with the intrinsic vibration of a molecule. The electric field strength of the incident light oscillates over time, t , and is described by Equation 1.2,

$$E = E_0 c \cos(2\pi\nu_0 t) \quad 1.2$$

where E is the strength of the electric field, E_0 is the maximum field strength (the amplitude of the oscillation) and ν_0 is the frequency of the photon.

On interaction with a vibrating molecule, the oscillating electric field induces a dipole within the molecule (see Figure 1.18). This excites the molecule into a higher energy state called a virtual or complex state. These virtual states are unstable so the energy is thought

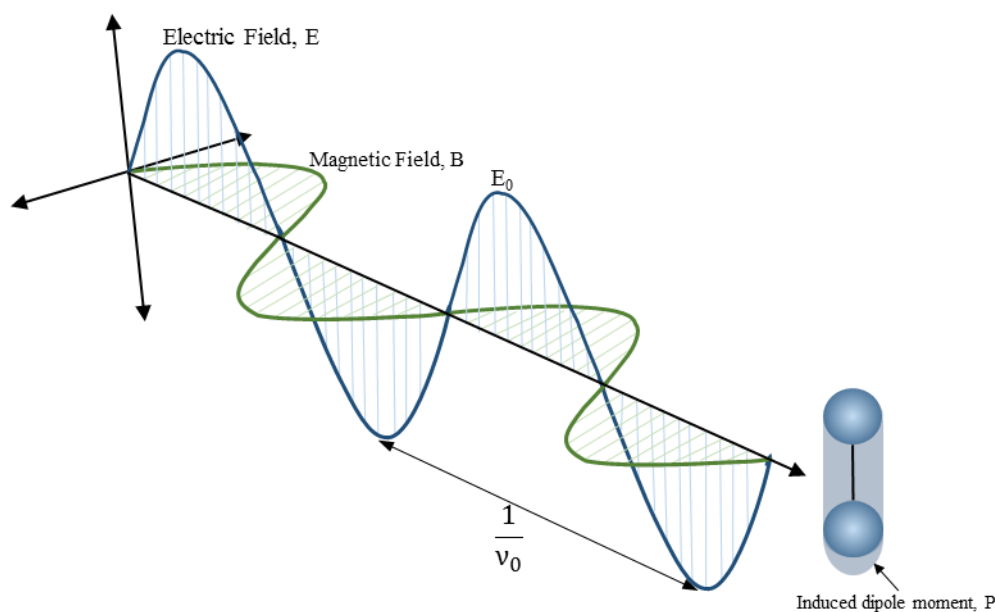


Figure 1.18: An illustration of photon in wave form, inducing a dipole (by influencing the charges) within the molecule.

to be instantaneously released as a photon, resulting in a scattering effect. The overall characteristics of such scattering effects (and the resulting molecular state) depend on the strength of the induced dipole. The strength of the dipole, P , is given by Equation 1.3

$$P = \alpha E \quad 1.3$$

where α is the polarizability of the molecules, a measure of molecular (electrons- nuclei system) flexibility, i.e. the amount of electron cloud distortion. Equation 1.3 can be rewritten (see Equation 1.4), by substituting the expression for E given by Equation 1.2,

$$P = \alpha E_0 \cos(2\pi\nu_0 t) \quad 1.4$$

The polarizability of the molecule, α , changes as the induced dipole from the photon displaces the internal masses within the molecule. Equation 1.5 describes how the total α

(summed over all vibrational modes) depends on the displacement of a given molecular vibration,

$$\alpha = \alpha_0 + \left(\frac{\delta\alpha}{\delta q}\right)_0 q_0 + \dots \quad 1.5$$

where α_0 is the polarizability of a molecule at equilibrium (before it is modulated by the induced dipole caused by the incident light). In the case of this description, it is only necessary to consider the first vibrational state (ν_0).

By substituting Equation 1.5 into 1.4 and using trigonometry identities, the strength of the induced dipole moment becomes,

$$P = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left(\frac{\delta\alpha}{\delta q}\right)_0 q_0 E_0 [\cos(2\pi(\nu_0 - \nu)t) + \cos(2\pi(\nu_0 + \nu)t)] \quad 1.6$$

Equation 1.6 incorporates three separate terms, each describing a type of oscillating dipole induced in the molecule and each contributing to the total dipole strength. The first term describes the oscillating dipole that arises without a change in reduced mass displacement, q , and therefore a change in polarizability. In this case, the photon electric field only distorts the electron cloud of the molecule. The cloud quickly relaxes within a few picoseconds (Ferraro and Nakamoto, 2012) back to its original state and light is scattered with the frequency ν_0 (see Figure 1.19). This process is known as Rayleigh scattering.

In contrast, the second and third terms in Equation 1.6 include a change in polarization term, $\left(\frac{\delta\alpha}{\delta q}\right)_0$, and therefore describe a much rarer case in which the photon is able to induce a dipole that alters the polarizability of a molecule (by causing a displacement in the reduced mass of the system). This additional movement of the nuclei is described as a change in vibrational state for the molecule and the resulting dipole will oscillate at a frequency different to ν_0 (the incident photon frequency). If the molecule is excited into a higher vibrational state compared with its original (see Figure 1.19), the dipole will oscillate with a frequency of $\nu_0 - \nu$, and the emitted photon will be seen to lose a

noticeable fraction of its initial energy during the scattering process (inelastic scattering). This process is known as Stokes Raman scattering.

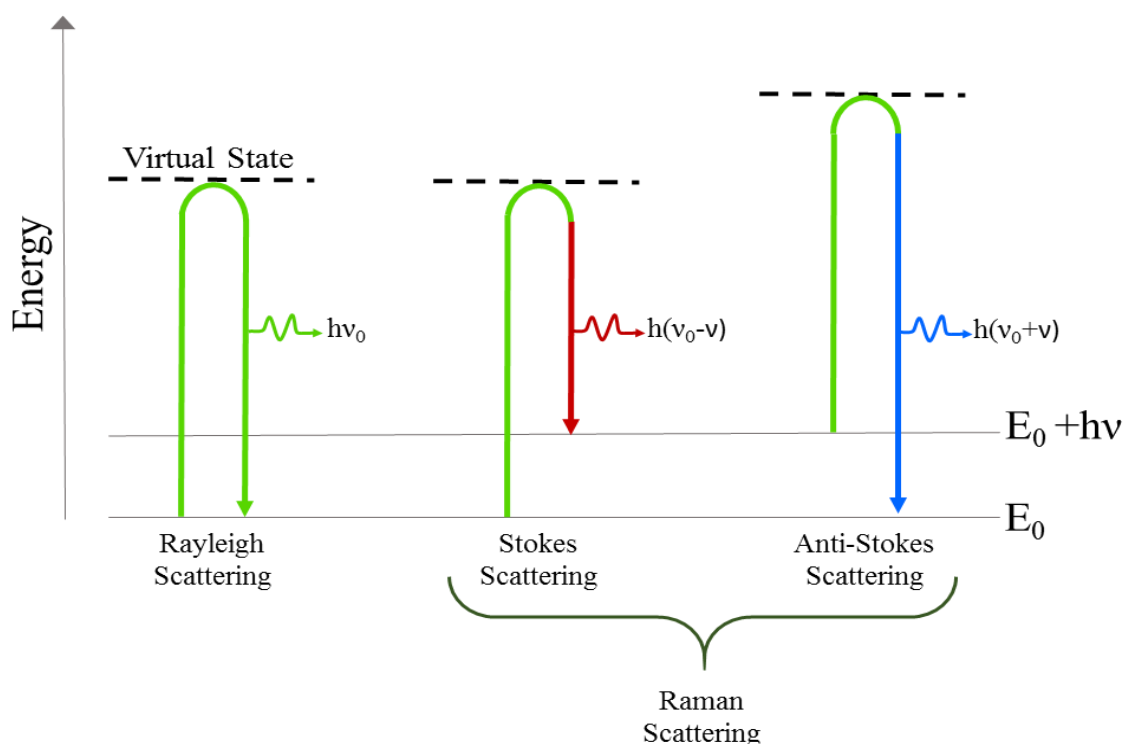


Figure 1.19: A Jablonski diagram illustrating the energy levels involved in Raman and Rayleigh scattering.

If the molecule's final vibrational state is lower in energy than its original state then the scattered photon will gain energy from the interaction and will have a frequency of $\nu_0 + \nu$, as indicated by Figure 1.19. This process is known as Anti-Stokes Raman scattering, and occurs less frequently than its Stokes counterpart, as it requires the molecules to originally be in an excited state. The population of molecules in an excited state is proportional to temperature according to Boltzmann's distribution (Long, 1977).

As stated earlier, the intrinsic oscillation of a molecule, ν , is governed by the fundamental characteristics of the material. Therefore, the change in photon frequency, due to the Raman Effect, reflects these characteristics and if measured can indicate the presence and properties of a particular molecule.

Although it is not evident from Equation 1.6, α_0 is generally significantly larger than $\left(\frac{\delta\alpha}{\delta q}\right)_0$ (McCreery, 2005), therefore Raman scattering is inherently weaker than Rayleigh

scattering, with only 1 in 10^7 photons scattering inelastically (Lewis and Edwards, 2001). A full quantum mechanical description of the Raman Effect (which is beyond the scope of this thesis but was developed by (Szymanski, 1967)) also highlights that the intensity of the Raman emission is proportional to the excitation wavelength, λ , according to the relation $I \propto \lambda^{-4}$. That is, ultra-violet excitation photons generate stronger Raman emission scatter than visible photons. However, the increased energy incident on the molecule may result in degeneration and can lead to an increase in fluorescence emission (Villar, Edwards and Worland, 2005).

Fluorescence is a photon absorption/emission process that occurs if the energy of an incident photon matches the energy gap between a molecule's original state and an excited electronic state (see in Figure 1.20). Because of the larger energies involved, the fluorescence process can heavily obscure a Raman spectrum. However, since the process involves the absorption of a photon (rather than scattering), the time scales for fluorescence emission are of order nanoseconds to microseconds (depending on the energy gap involved) (Pawley, 2010), compared with a picosecond timescale for Raman scattering. This time scale difference means that the fluorescence emission from a sample can be temporally isolated if a Raman spectrometer can detect the Raman signal on a

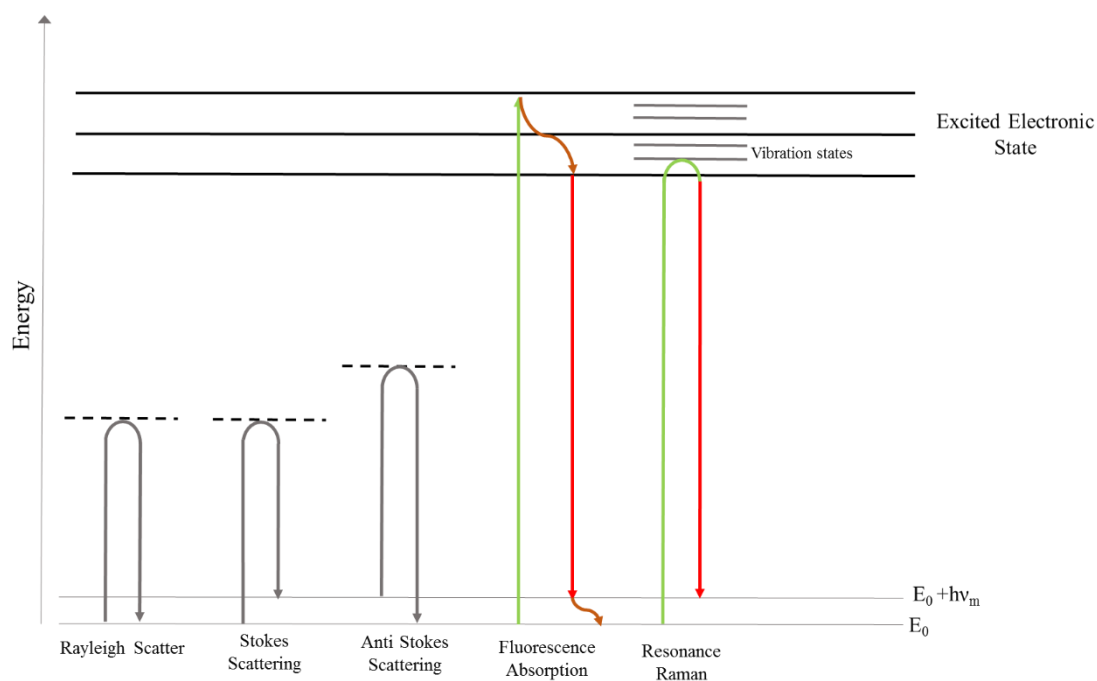


Figure 1.20: A Jablonski diagram showing the energy levels involved in Rayleigh, Raman scattering, Fluorescence absorption and Resonance Raman scattering.

picosecond or nanosecond time scale (i.e. before the fluorescence emission reaches the instrument (Carter *et al.*, 2005)).

An excitation photon with energy corresponding to a Raman mode (vibration state) within an excited electronic state can greatly enhance the intensity of the scattering process (shown by the Jablonski diagram in Figure 1.20). This is known as the Resonance Raman Effect and the resultant scattered light is 10^6 times more intense than non-resonance Raman emittance (Marshall *et al.*, 2007). This phenomenon can be utilised by selecting (or fine-tuning) the excitation frequency, ν , so that it coincides with the energy gap between the lower vibration states and those in an excited electronic state (Asher and Bormett, 2000).

Figure 1.21 shows a schematic of a typical Raman spectrometer. To induce Raman emission for spectroscopy applications, samples are usually irradiated by a laser. A laser provides an intense source of monochromatic photons, which not only controls the ν_0 parameter, but will also maximise the Raman emission. The scattered light is collected and the intense Rayleigh scattered light is filtered out. The inelastically scattered light is diffracted into its component wavelengths by a grating and the resulting diffraction order is focused onto a detector (which determines the number of photons at each wavelength). A Raman spectrum is then obtained by plotting the intensity of the detected signal (or an equivalent measurement) versus wavelength. Since the emitted photon frequencies, ν , are a small shift from the excitation frequency, ν_0 , the scattered photon frequencies are often

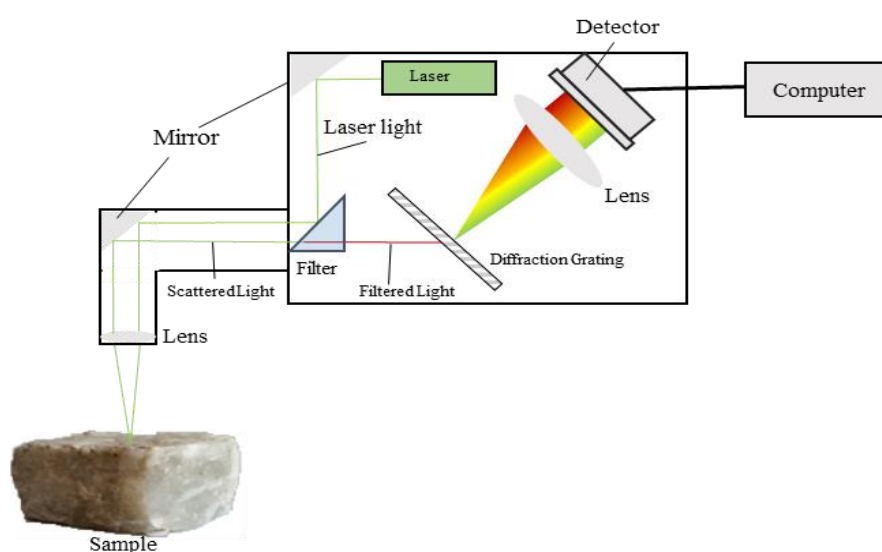


Figure 1. 21: A diagram depicting the simplified layout of a Raman Spectrometer.

given in wavenumber offsets (with units' cm^{-1}). The photon frequency (or wavelength) is converted to a relative wavenumber using Equation 1.8,

$$\text{wavenumber } (\text{cm}^{-1}) = \frac{\nu_0 - \nu}{100} \quad 1.8$$

or Equation 1.9

$$\text{wavenumber } (\text{cm}^{-1}) = \frac{\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}{100} \quad 1.9$$

where λ_0 and λ are the excited wavelength and emitted photon wavelength respectively. The factor of 100 has been included to convert from m^{-1} to cm^{-1} . It should be noted that Equation 1.8, the speed of light, c , has been omitted for convenience since the absolute photon frequencies are large in comparison to the observed Raman shift.

Figure 1.22 shows an example of a Raman spectrum obtained from a geological sample. The bands (peaks) arise from the magnitude of photons scattered as the molecules enter their fixed vibrational states. The position of the peaks in the spectrum (i.e. the frequency of the scattered photon) are used to determine information about the molecular bonds present in the sample.

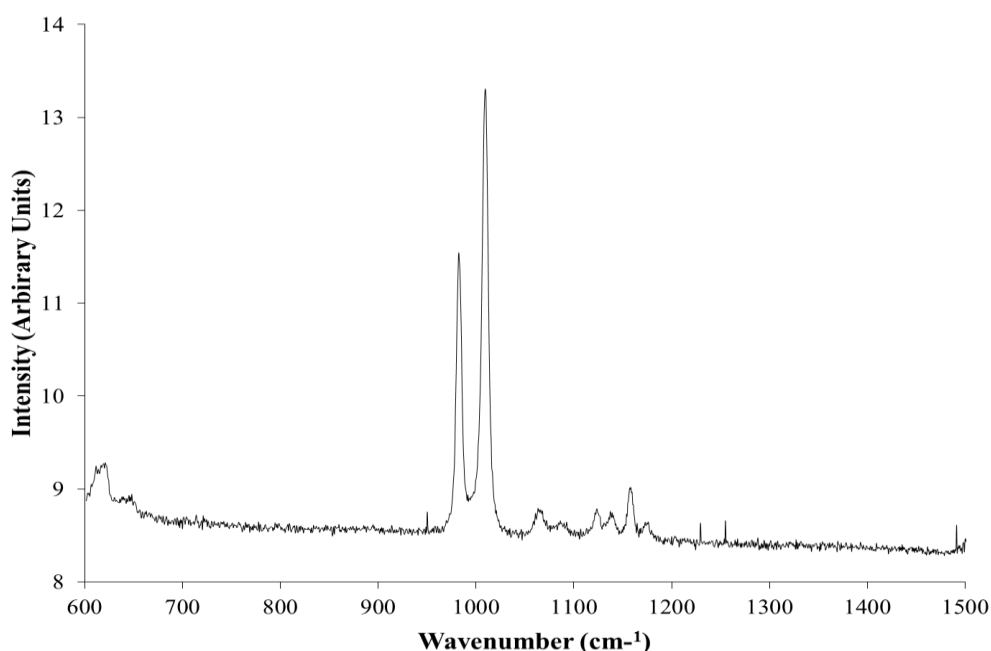


Figure 1.22: An example of a Raman spectrum obtained from a sample of anhydrite.

The Raman technique has many advantages over other analytical techniques; it is fast, generally non-destructive and samples do not need to be prepared (Lewis and Edwards, 2001). The technique is also applicable to solids, liquids and gasses and its sharp distinctive bands (peaks) lead to a less ambiguous analysis, compared to infra-red spectroscopy (Lewis and Edwards, 2001). As this section has highlighted, the intensities of the Raman bands do not directly relate to the abundance of the mineral in the sample, but depend on many other factors, including the Raman cross section, which is discussed in detail in Chapter 3, Section 3.2.3. Instead, the relative peak intensities are often measured and can provide information on covalent bonds, crystal orientation and structural ordering in the crystal lattice (Haskin *et al.*, 1997).

1.3.2 STAND-OFF RAMAN SPECTROSCOPY

Over the last few decades, Raman spectroscopy has become a well-established and powerful tool in the fields of biology, chemistry, archaeology, pharmaceuticals, forensic science, security/defence and the nuclear waste industry. In many of these fields, the technique is applied in close proximity to the sample and can be used to investigate a material on a microscopic scale. However, in 1974, the idea of performing Raman spectroscopy from a remote distance was considered theoretically and demonstrated experimentally for the first time through the measurements of nitrogen in the atmosphere (Hirschfeld, 1974). Soon after, the technologies associated with remote Raman spectroscopy were matured within the field of Lidar for atmospheric mapping using ground based, static instrumentation and systems at intermediate distance above ground (Leblanc, McDermid and Walsh, 2012). Klein *et al.* (2004) provide a detailed discussion of the potential of Raman Lidar systems in low earth orbit.

The components of a stand-off Raman instrument share similarities to those of a conventional, in situ instrument. These include: a laser excitation source, collection optics, a filter to obstruct Rayleigh scattered light, a diffraction grating with accompanying optics and a detector (usually a charge coupled device (CCD)). In 1992 a small stand-off instrument was developed to detect organic and inorganic molecules in remote material. The design included a larger collection aperture than that of an in situ or microscopic Raman system (which offers a greater signal throughput from the sample)

and used a low powered, continuous wave laser (Angel, Kulp and Vess, 1992). The structure and configuration of Stand-off systems are discussed in Chapter 2, Section 2.1.

1.3.3 OPTIMISATION FOR PLANETARY EXPLORATION

Stand-off Raman spectroscopy has already proved to be a valuable tool in the fields of geology and mineralogy and for the past decade efforts have focused on adapting the instrumentation for planetary exploration. In 2003, Sharma et al. (2003) incorporated components similar to those developed previously for planetary missions (such as a small pulsed Nd:YAG laser and a 5-inch diameter telescope). This system successfully detected hydrated substances, carbonates and silicates at distances of up to 66 metres.

More recently, Carter et al. (2005) demonstrated that the overall performance could be improved by coupling a pulsed laser with a gated detector. The combination can achieve a significantly greater signal-to-noise ratio through the temporal isolation of background signal associated with fluorescence. As discussed in Section 1.3.1, the fluorescence process is significantly slower than Raman scattering due to the full absorbance of an incident photon. The timescale for the emission of a fluorescence photon is several orders of magnitude longer than the Raman scatter timescale which is typically 10^{-13} s (Bozlee *et al.*, 2005; Misra *et al.*, 2005). A 10 ns gating of the signal after each laser pulse has been shown to effectively reduce the fluorescence background (Misra *et al.*, 2005). Current stand-off systems use intensified CCDs (iCCDs) in conjunction with pulsed lasers since they not only intensify the signal but also allow high precision gating (Wiens *et al.*, 2005). A gated detector system also allows the instrument to operate in high ambient light conditions relative to the total signal (such as outside in the daytime) since the time in which background light can be detected is greatly reduced (Sharma, 2007).

Furthermore, a number of studies have compared different system configurations. Sharma et al. (2007) compared direct coupling of the system collection optics to the spectrograph with the use of fibre optics. Fibre optic coupling offers wider flexibility within the system (i.e. the collection optics can be situated some distance from the spectrograph and have freedom to move independently), but Misra et al. (2005) demonstrated that signal losses are greater compared to the directly coupled approach. Further to this, Sharma et al. (2007) compared two different geometric configurations; an oblique and co-axial. These

geometric configurations, along with a comparison of other subsystem alternatives are discussed in detail in Chapter 2.

Stand-off Raman spectroscopy has also been utilised in conjunction with complementary analytical techniques such as LIBS. LIBS is a laser based elemental identification technique which requires many of the instrumental components utilized by a Raman spectrometer (Wiens et al. 2005; Sharma et al. 2007; Rull et al. 2011). LIBS instruments measure the photon emission resulting from induced plasma. Consequently, a significantly greater energy density at the sample is required compared to that used for Raman excitation. For example, Wiens et al. (Wiens *et al.*, 2005) used a pulsed Nd:YAG laser for both techniques (operating at 1064 nm for LIBS and 532 nm for Raman spectroscopy), but to perform LIBS, the laser light had to be focused onto a smaller spot (<1 mm) on the sample (Wiens *et al.*, 2005).

1.3.4 IN SITU AND STAND-OFF RAMAN SPECTROSCOPY FOR FUTURE PLANETARY EXPLORATION MISSIONS

Over a decade ago, Raman spectroscopy was highlighted as a potential analytical tool for exploring the lunar surface. Wang et al., (1995), used a fully miniaturized (<20 cm³) instrument to demonstrate that common minerals and organics could be detected on the surface of the Moon. Minerals such as pyroxene are complex but are fundamentally important to understanding the formation history and past geological processes of the Moon. It was demonstrated that the clear and unambiguous properties of the Raman spectra obtained from such materials, such as sharp, non-overlapping peaks, are ideal for identifying silicates, carbonates, phosphates and sulphates (Wang, Jolliff and Haskin, 1995). Other studies related to the analysis of Apollo samples with Raman spectroscopy instruments, have demonstrated it is possible to easily detect olivine, feldspar and pyroxene (Ling, Wang and Jolliff, 2011).

Further work by Wang et al. (1994) showed that the strong bands produced by SiO₃, CO₃, SO₄, or PO₄ shifted depending on the cation variation within the material. For example, it was demonstrated that the ratio of enstatite, ferrosilite, diopside and hedenbergite can be deduced from the acquired Raman spectra (Wang et al. 1994). The study also showed that pyroxene crystal structures are easily discernible due to the appearance of a double

band at 670 cm^{-1} and a single band at 650 cm^{-1}) for orthopyroxene and clinopyroxene respectively. In addition, small sharp bands observed in lunar spectra were demonstrated to arise from microcrystal structures within lunar glasses. Spectra given by Wang et al., (1994) also showed that the glass content of lunar regolith can reveal important information about the chemistry, shock and radiation alteration history of the material.

The instrumentation required to detect olivine, pyroxene, pyroxenol, feldspar and other minerals in the studies described here, were not dissimilar to the stand-off systems described in Section 1.3.3 (Wang, Jolliff and Haskin, 1995). The spectrograph utilised a 532 nm laser and collects scattered signal at an angle of 180° . The collection optics are coupled to the spectrograph via an optical fibre, containing a holographic grating and a CCD detector. It is therefore reasonable to assume that a stand-off Raman system would be able to successfully detect these minerals from a remote distance if the signal-to-noise levels at the detector are adequate. In addition, techniques such as Raman spectroscopy (stand-off Raman spectroscopy in particular) could be relied upon to provide fast and remote identification of potential resource sites to aid in future ISRU.

In the last 10 years, numerous studies have shown that Raman spectroscopy is well suited as an analytical tool for Mars exploration. Hutchinson et al. (2014) and Jehlička & Edwards (2014) have given extensive reviews on the adaptation of Raman spectroscopy to planetary exploration and for the analytical study of extremophiles respectively. For the first time in 2020, ESA will fly a Raman spectrometer as part of a rover payload to the surface of Mars as part of the ExoMars rover mission. The Raman Laser Spectrometer (mentioned in Section 1.1.2) is a compact, robust, low power, low mass instrument dedicated to identifying biological signatures and mineralogical materials. The spectrometer uses a 532 nm Diode Pumped Solid State (DPSS) continuous laser. The laser is focused into a $50\text{ }\mu\text{m}$ spot on the target sample with a total irradiance of $0.6\text{--}1.2\text{ kWcm}^{-2}$. The collection optics are coupled to the spectrometer via an optical fibre with a diameter of $50\text{ }\mu\text{m}$. The spectrometer includes a holographic transmission grating, which disperses a single diffraction order (ranging from 100 to 4000 cm^{-1}) onto a thermoelectrically cooled, charge coupled device (CCD) detector. The CCD is a back-illuminated, 4-phase, non-inverted mode device (CCD230) manufactured by e2v technologies with 528 by 2048 , $15\text{ }\mu\text{m}$ pixels (Ingley et al., 2014).

The Mars 2020 Science Definition Team listed Raman spectroscopy as a key component of the payload for fine scale mineralogy and the detection of organics (Mustard *et al.*, 2013) on Mars. As a result, an in situ Raman spectrometer was selected for the Mars 2020 payload. The Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument (Beegle *et al.*, 2016) will be mounted on the arm of the rover. The instrument utilises a deep Ultra-violet laser operating at 248.6 nm. At this wavelength, the laser induces fluorescence emission from carbon and organic molecules containing aromatic rings (which become detectable even in small quantities) and is able to infer the nature and distribution of organic material in the Martian soil. The Raman and fluorescence emissions are collected by the same detector since their respective spectral regions of interest are ~251-275 nm and ~275-400 nm (Beegle *et al.*, 2014).

In addition to SHERLOC, the JPL managed, Mars Microbeam Raman spectrometer (MMRS) was proposed for the Mars2020 flight project. The MMRS prototype is composed of an arm-mounted optical probe coupled to a low mass spectrometer via an optical fibre (Wang *et al.*, 2016). The instrument uses a 532 nm, DPSS laser source and provides 10 mW of power to the sample surface. The spectrometer includes a holographic grating and a cooled CCD detector. The device has 1088 by 1088, 12 μm pixels, resulting in $<7\text{ cm}^{-1}$ spectral resolution (Wang *et al.* 2003). The spectrometer covers two separate spectral ranges: 200–1800 cm^{-1} for the characterization of minerals and graphitic carbon, and 2500–4000 cm^{-1} for the detection of organic functional groups and water (see Wang *et al.* 2003). The system is also capable of line scanning and can obtain over one hundred spectra from a 1.2 cm line on a sample surface.

However, in situ instruments such as this rely on sample collection systems to provide material to the system and since organic molecules are a rarity on the surface of Mars, an efficient and effective sampling method is crucial to obtaining the maximum amount of information from a target sample. Currently, rover sampling is limited to moving the rover and manipulating the collection systems. Stand-off Raman spectroscopy may change this. By retrieving detailed information from a remote distance, a rover has the ability to assess a region of interest without the need to re-locate. This will not only save time but also system power. Using stand-off Raman spectroscopy, rovers will have the ability to analyse inaccessible regions, such as cliff edges and caves.

Sharma et al. (2007) have performed stand-off Raman under simulated Martian conditions (around 933 Pa) using a combined Raman/LIBS system. Spectra were obtained from calcite, gypsum and sulphur at a distance of 8.6 m. Stand-off systems have also been successfully tested at Mars analogue sites, such as the Arctic. Rull et al. (2011) successfully obtained spectra from ice at a distance of 120 m clearly showing vibrational differences between different ice structures. As a result of this extensive testing and optimisation, Stand-off Raman spectroscopy has been identified as an essential reconnaissance tool and as a primary science instrument for future Mars exploration (Clegg, Wiens and Maurice, 2014). In 2015, a stand-off Raman system (SuperCam) was selected, along with SHERLOC, as part of NASA's Mars2020 mission payload. SuperCam is a remote system that integrates Raman, LIBS, time resolved fluorescence, visible and infra-red spectroscopy and colour remote microimaging for context colour imaging (Clegg *et al.*, 2016). The instrument is based on the ChemCam (Mars Science Laboratory) structure with subsystems divided into two units; a mast mounted unit and a body unit. The mast mounted unit includes a 110 mm telescope and an Nd:YAG laser which operates at 1064nm for LIBS and at a frequency doubled wavelength of 532 nm operation for Raman and fluorescence spectroscopy. The Mast also includes an IR spectrometer, a Remote Micro-Imager (RMI) camera and associated electronics. The body unit couples to the mast unit via an optical fibre. The body unit includes two reflection spectrometers (also based on ChemCam heritage) and a transmission spectrometer (which utilises an intensified CCD). The ICCD gate lengths are 100 ns and the spectrometer operates over a distance of 7-12 m (Wiens *et al.*, 2016).

As well as being an ideal tool for analysing the Martian surface, Raman spectroscopy has also been identified as a powerful tool for the exploration of Venus. As previously described (Section 1.1.3), spacecraft can only survive on the surface of Venus for a short amount of time (around 60 minutes on average) due to the particularly hostile environment. Raman Spectroscopy has many advantages over other techniques in this type of mission environment. The acquisition of definitive, unambiguous spectra is a rapid process (<1 minute per spectrum - see (Wang, 2009)) that does not require sample preparation. This also means that the technique can be performed through a window and can be used to investigate atmospheric composition. Raman spectroscopy is also sensitive to abundant elements on Venus, such as sulphur. The form and distribution of sulphur is paramount to our understanding of the Venusian sulphur-cycle (Wang, 2009). Wang

(2009) showed that the ratio of sulphur mixtures can be readily observed in igneous rock formations using Raman spectroscopy.

Stand-off Raman spectroscopy has also been demonstrated on samples under Venusian conditions (approx. 95 atm pressure and a temperature of 423 K) at distances of 1.5 and 9 metres through a sapphire window (see Sharma et al. 2010). There were no obvious signs of line broadening due to the increased pressure but the dehydration and decarbonation of certain minerals was observed.

Raman spectroscopy is not only well suited to geochemical and mineralogical investigation on planetary bodies such as Mars, the moon and Venus, but also the icy moons of the solar system. In light of the proposed mission to Europa (see Section 1.2.4), Sobron et al. (2013) suggested that in situ (and stand-off) spectra from a combined Raman/LIBS instrument would provide an extensive elemental and molecular picture of sample composition and structure under cold temperature conditions. The acquired spectra provide information on mineral phases, as well as bulk and trace elemental components of water ice mixtures with salts and organics at a temperature of -50°C. In addition, Sharma et al. (2014) 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.

Wiens et al (2016) have suggested that slight modifications to the ChemCam structure (to include a remote Raman system) could be a powerful tool in the detection of carbon and nitrogen containing ices and water ice for future missions to Titan. Jehlicka et al (2010) also suggested that miniaturised, portable Raman spectrographs are capable of detecting the presence of nitrogen-containing organic compounds and biomolecules under low temperature conditions. Since Raman spectroscopy is sensitive to molecular vibrations such as S-S, C-H, C-O, C-N, N-O, N-H, many of which appear in complex biomarker molecules such as protein, biological pigments and amino acids, Sobron et al. (2014) describe the development of an underwater Raman spectrometer that could be used to investigate submerged material.

In light of the past and future missions described in this chapter this thesis focuses on the key role that Raman spectroscopy is likely to play in the exploration of various planetary bodies and the knowledge that it will provide.

This thesis presents the development and optimisation of both in situ and stand-off Raman instrumentation for planetary exploration. Firstly, Chapter 2 gives a review of the technology currently available for Raman instruments and the performance enhancements they theoretically provide. Chapter 3 of this thesis then describes the hardware system developed based on the Raman instruments described above in section 1.3.4. Chapter 3 also describes a detailed model of the developed Raman system and outlines how the performance of instrument can be effected by the optical configuration, excitation source, target sample, operating modes and environmental conditions.

Chapter 4 give details on a real-time simulation based on the radiometric model described in chapter 3. The chapter then presents a number of instrument optimisation recommendations based on the results generated by the simulation.

Chapter 5 describes a software interface that was developed as a tool to optimise instrument data acquisition strategies and provide control of support for instrument hardware. The chapter then presents a set of throughput measurements acquired to verify the radiometric model. Finally the chapter details 3 instrument performance verification studies that concern instrument spectral resolution, working at a stand-off distance and the effect of radiation damage.

Chapter 6 presents two analytical studies that demonstrate the performance of flight-representative Raman instruments when acquiring data from standard samples as well as a Mars analogue sample.

Finally, Chapter 7 presents the spectra obtained using in situ Raman instrumentation during two field campaigns. The chapter then presents the theoretical performance for various alternative systems (that vary in configuration and operating mode).

2 INSTRUMENTATION

There are four main subsystems in a Raman spectrometer: an excitation source, collection optics, a spectrograph and a detector. In this Chapter, the functionality of each system is described in detail and the fundamental performance requirements are summarised. Consideration is also given to the maturity level of recent technical developments that provide the best instrument performance, especially with regard to their suitability for space applications. This section also describes how each subcomponent can be optimised or adapted in order to perform Raman spectroscopy at stand-off distances. In particular, the chapter focuses on the detector system and the operating modes that will be critical in the system optimisation process.

2.1 STAND-OFF BENCHTOP SYSTEM

2.1.1 EXCITATION SOURCE

When choosing an appropriate excitation source, it is important to consider several fundamental aspects of the Raman spectroscopy technique. For example, Raman scattering is measured as a shift in photon wavelength with respect to the wavelength of the excitation source, therefore it is essential that the excitation source is monochromatic (or has a line width $<0.05\text{nm}$), with a peak wavelength stability of less than 0.05nm drift (Lewis and Edwards, 2001). Otherwise, the width of the observed Raman bands would be limited by the broad range of excitation wavelengths (although it should be noted that the effects of line broadening and shifting can be minimised through effective calibration and data processing – see Chapter 3). Furthermore, due to the fact that the Raman effect is fundamentally a weak scattering process (Smith and Dent, 2013), the excitation source

needs to be intense, producing a sufficient energy density at the sample to maximise the Raman scatter (this requirement is even more important when considering stand-off Raman spectroscopy systems). However, the precise amount of power required to induce a sufficient Raman signal is highly sample dependent and it is important to account for the fact that the intensity at the surface of the sample should not exceed the damage threshold of the material (i.e. the intensity at which local heating causes breakdown of the molecular structure of the sample). It should also be noted that a higher energy density also stimulates an increase in fluorescence signal.

These specific requirements mean that laser light sources are the preferred choice of excitation for most Raman spectroscopy applications. Lasers primarily produce monochromatic and coherent light with a typical line width of less than 0.05nm (Duarte 2013, Continuum 2002). For optimum wavelength stability, it is important to ensure that the temperature of the laser does not drift (typically needing to be controlled to within 0.01°C in order to achieve a wavelength stability of <0.05nm) (McCreery, 2005; Duarte, 2015). The effects of wavelength drift can be reduced by implementing optical components that maximise the output of one particular wavelength i.e. filters and gratings (Menzel, 1994). Recent advances in laser technology mean that powerful lasers can be stabilised and operated efficiently at relatively low cost. A number of different laser types exist and their individual characteristics, advantages and disadvantages are discussed below and summarised in Table 2.1.

GAS-LASERS

Gas lasers, such as Helium-Neon (He-Ne) lasers, are some of the most common and inexpensive lasers available (that meet the tens to hundreds of milliwatts power requirement required for Raman spectroscopy) (Lewis and Edwards, 2001). A He-Ne laser consists of a gas cavity that contains Helium and Neon at a ratio of 10:1 (Sharma, 2005). To start the lasing process, Helium is pumped to an excited state using an electrical discharge. A potential difference of 8-10kV (Gupta and Khare, 2014) is generated between an anode and cathode on either side of the cavity. Electrons, accelerated between the electrodes, collide with the Helium, pushing the molecules into long lived metastable states (2^3S and 2^1S) (Nagourney, 2014). This is known as a population inversion since there are more molecules occupying higher energy states than there are in the lowest energy states (in which they would naturally reside). Once in these higher energy states,

the Helium molecules cannot decay to the ground state as the transition is forbidden according to selection rules. The 2^3S and 2^1S (20.61eV and 19.78eV) energy levels of Helium reside very close to the 2S and 3S (20.66eV and 19.78eV) (Gåsvik, 2003) excitation levels of Neon and since these states are so close in energy there is a high probability of energy transfer through a collision between Helium and Neon. This process promotes the Neon atoms to a higher state and after a short time, the Neon molecules will decay to a lower state, emitting a photon of energy equal to the energy difference between the two states.

The most common Neon decay transitions and the wavelengths of the photons produced are listed below:

- 3s-3p: 339nm
- 3s-2p: 632.8nm (most commonly used)
- 2s-2p: 151nm

These transitions are also highlighted in Figure 2.1. To complete the lasing cycle, the neon atoms transition from the 2p energy state to the 1s energy state through spontaneous radiative emission (a fast transition compared with the stimulated transitions). The 1s to ground transition then occurs through radiative diffusion into the walls of the chamber, thus completing the lasing cycle (Rogers, 2008).

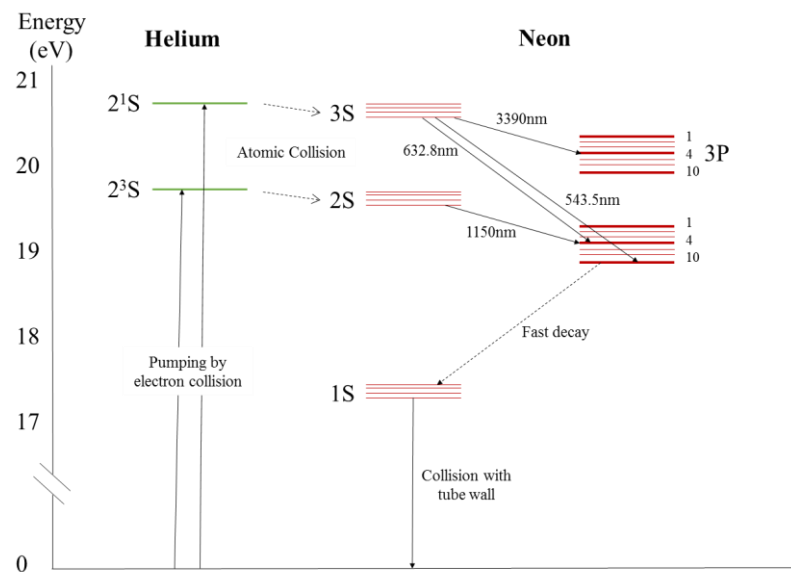


Figure 2.1: A diagram illustrating the energy levels involved in the lasing process of a He-Ne laser.

If a stimulated photon is released along the axis of the cavity it will be repeatedly reflected between two mirrors located at either end, which will stimulate emission of photons from other atoms (Kane, 2009). One of the mirrors has a 100% reflectance while the reflectance for the second mirror is ~99% (which is where the laser light is emitted from the cavity) (Gupta and Khare, 2014). Laser processes such as this generate a constant source of monochromatic, coherent light, usually described as a continuous wave (CW) source. In addition to the laser wavelengths given here, the He-Ne plasma inside the chamber emits atomic lines which must be blocked in order to prevent interference with the laser radiation (Ferraro and Nakamoto, 2012).

A typical He-Ne laser cavity is 20-50 cm long and 1-2 mm in diameter (Gupta and Khare, 2014). The small volume makes the final decay transition of the lasing cycle (the 1S to ground energy transition, as seen Figure 2.1) frequent enough to maintain the cycle, producing a continuous wave laser. The smaller cavity makes He-Ne lasers less expensive compared to other laser types and recent developments in cathode technology have extended the laser system lifetimes to exceed 10000 hours (Ready, 2012). Unfortunately, the small cavity produces a relatively small amount of power (5-50mW) (Gupta & Khare 2014, Pawley 2010). However, this does reduce the complexity of cooling mechanisms, requiring only air-cooling to maintain wavelength stability.

ARGON ION LASERS

In a similar fashion to He-Ne lasers, Argon lasers also consist of a chamber filled with gas. The Ar gas is ionised using a strong electric discharge (50A, 100V DC) (Nagabhushana, 2010). As a result, the Ar ions are pumped from the atom's ground state to a higher energy state in two stages, as indicated in Figure 2.2. In the case of Argon this is the 4P state at ~35eV (Nagabhushana, 2010). Two decay transitions follow, both from 4P to 4S, but due to the high degeneracy of the 4p and 4s energy levels, an Ar laser can produce many different wavelengths. Figure 2.2 shows the multitude of transitions that can occur from the $4P^2$ and $4P^4$ states to the $4S^2$ state. The stimulated emission is followed by two radiative decay transitions (from the $4S^2$ state to the argon ion ground state and the subsequent transition to the argon atom ground state) which completes the lasing loop (Avadhanulu, 2001).

The two most common decay transitions, however, are those that produce 514.5nm and 488nm photons (Svelto, 2010). Argon lasers can produce between 50 and 100mW of continuous wave emission (Ferraro and Nakamoto, 2012). Lasers of this power are short lived (5000hrs) and usually require water cooling, making them large (50-100cm) and expensive (Turner, 2013). Since Ar lasers are capable of emitting light in the UV, additional costs arise from the need for a discharge tube that can withstand high temperatures. Such tubes are often made of BeO, which has a particularly high thermal conductivity (Turner, 2013).

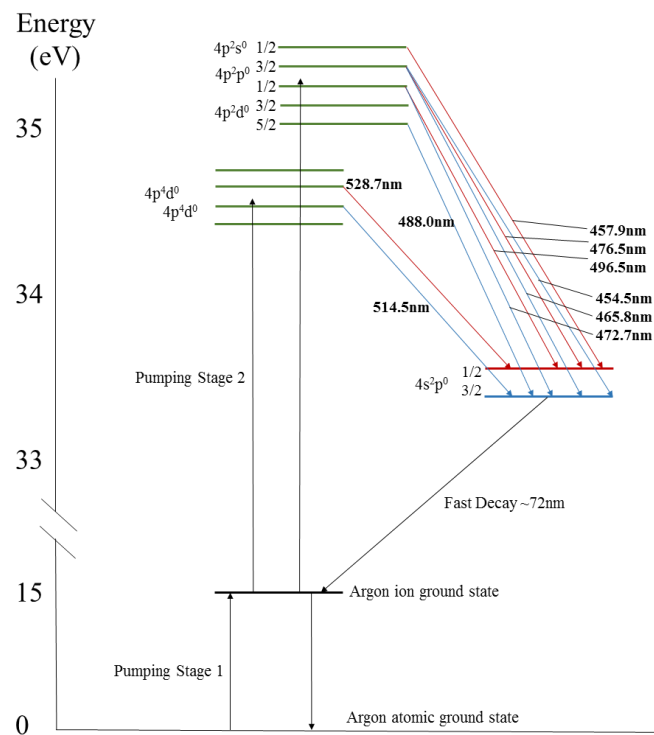


Figure 2.2: The argon laser is capable of emitting laser light of many wavelengths. Desired wavelengths are usually selected using filter, diffraction grating or prisms (Demtröder 2002). Stimulated emission of 351nm can also be achieved by using Ar⁺⁺ ions (William 1960).

SOLID STATE LASERS: DIODE LASERS

Monochromatic light can also be generated by a semiconductor p-n junction made of an alloy of aluminium and gallium arsenide (Abramczyk 2005). Figure 2.3 shows the structure of a diode laser. When a forward bias is applied, the energy gap associated with the p-n junction is reduced. As a result, charge carriers begin to build up at the edge of the junction. This concentration of charge carriers constitutes the required population inversion (Abramczyk, 2005). When the electrons recombine with the holes in the active

zone (the layer between the p and n-type materials), photons are emitted. Similar to the laser cavities described above, mirrors are placed at both ends of the semiconductor (perpendicular to the active region) (Joshi 2010). Consequently, any photons that are emitted parallel to the junction will be reflected back and forth within the cavity, stimulating further photon emission (Madou, 2011). Unlike the other types of laser, the emerging light is highly divergent so has to be collimated by a lens before it exits the laser structure (Kannatey-Asibu and Jr., 2009).

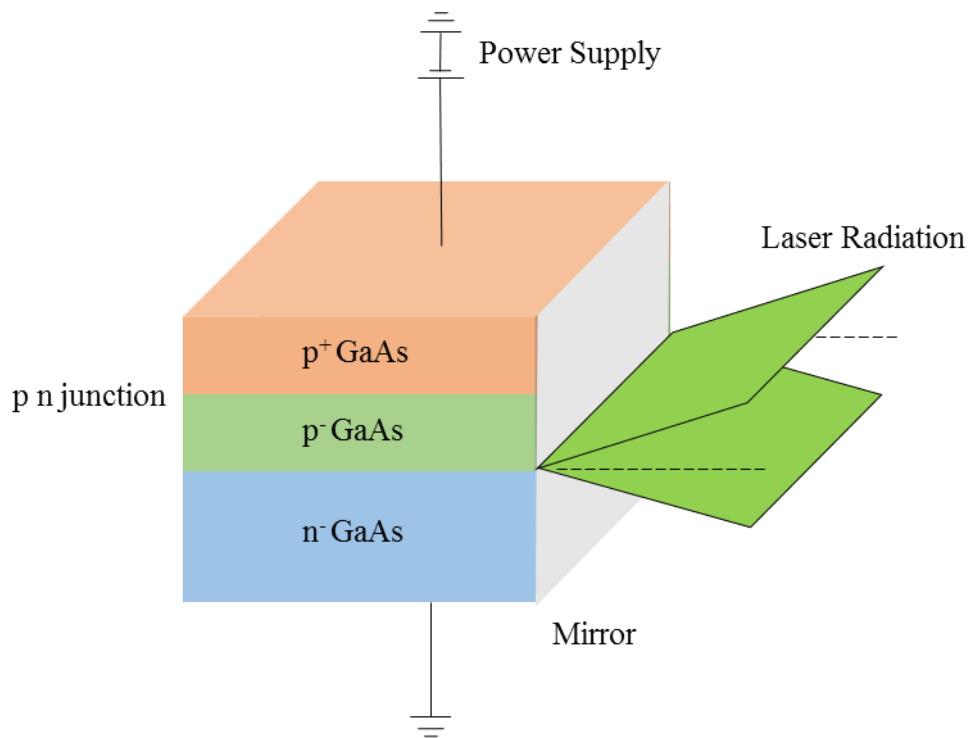


Figure 2.3: Simplified diagram of a diode laser structure.

Diode lasers can emit several different wavelengths (sometimes spontaneously) as photons of different wavelengths and direction compete for dominance in a single mode structure. To minimise the number of different output wavelengths, the diode is usually placed in an external cavity with a diffraction grating to restrict the unwanted resonating wavelengths (Loh *et al.*, 2006).

The wavelength and power produced by this type of laser depends on the semiconducting material. GaAs predominately produces 840nm light at a power of 5mW, while AlGaAs and GaInAsP generate wavelengths of 760nm at 50mW and 1300nm at 20mW respectively (Bakshi and Godse, 2008). These power outputs would not be appropriate for use in a stand-off Raman system as they would not produce a sufficiently strong

Raman signal that could be detected over a large distance. However, these low powered lasers would be sufficient for small in situ Raman instruments. A typical operating lifetime for a diode laser exceeds 15000hrs (Gupta and Ballato, 2006) and, coupled with their small size (a few centimetres in total), low powered diode lasers require minimum cooling and only consume 50W of power, making them very efficient. However, these lasers have a tendency to drift in wavelength although stabilisation of $\pm 5\text{nm}$ can be achieved with simple closed loop thermal controllers (Ronda, 2007).

SOLID STATE LASERS: Nd: YAG

To achieve laser powers in excess of those described above ($<100\text{mW}$), Nd: YAG lasers can be utilised. The Nd: YAG laser consists of an yttrium-aluminium-garnet (YAG) host crystal that has been heavily doped with Nd^{3+} ions to create a specific triplet geometry within the crystal. It is this geometry that allows a population inversion to occur in high energy complex states (states $4F_{5/2}$ and $2H_{9/2}$ in Figure 2.4). The energy levels created by the crystal geometry are shown in Figure 2.4. The laser process is based on four energy levels: two higher levels, from which electrons decay via stimulated emission (producing laser light), and two subsequent lower levels that provide fast transitions to ground to preserve the population inversion. In the standard mode of operation, the laser is pumped continuously to generate a continuous wave output with a wavelength of 1064nm (Telle, Ureña and Donovan, 2007).

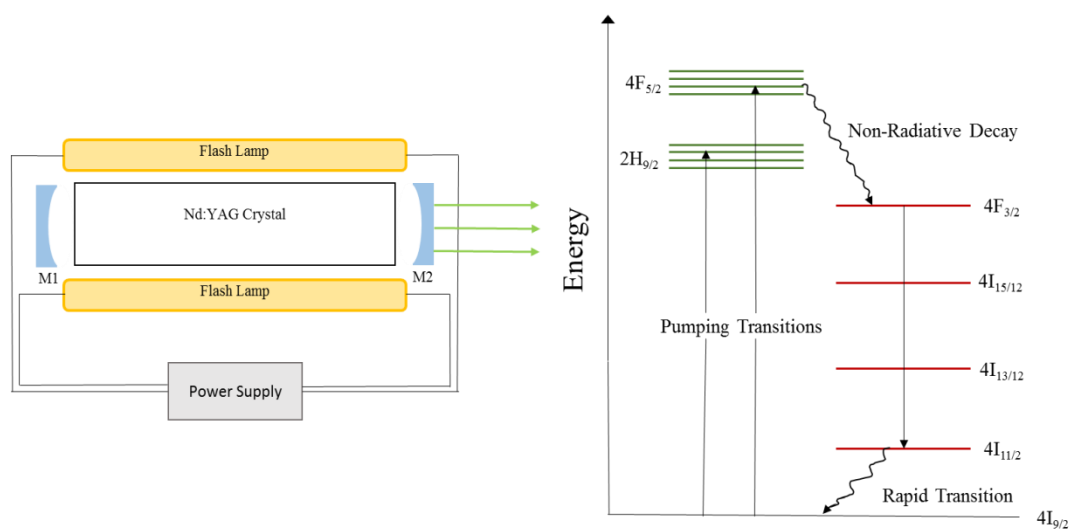


Figure 2.4: A schematic of the structure of a Nd: YAG laser (left) and a simplified illustration of the YAG crystal energy levels involved in the laser process, as well radiative transitions that occur within (right).

In the early versions of such lasers, the population inversion was achieved by pumping with flash lamps. However, flash lamps are normally large, slow and produce a significant amount of heat and therefore need to be replaced every 400-800 hours of operation (Pawley, 2010). Consequently, many Nd: YAG lasers are now pumped with a laser diode (see the section above) and are referred to as Diode Pumped Solid State (DPSS) lasers. Diode lasers are small (~12cm x 3cm x 4 cm) and do not require significant cooling (i.e. air cooling is sufficient). They are also considerably more efficient (>50%), because most of the light is concentrated onto the Nd:YAG crystal (Pawley, 2010). However, the integration of a diode laser does increase the overall cost of an Nd: YAG laser.

The main advantage that Nd: YAG lasers have over the other lasers described in this section is the ability to be frequency doubled to produce 532nm wavelength light using an additional crystal. The crystal used to accomplish this is usually a potassium titanyl phosphate (KTP) or a potassium titanyl arsenate (KTA) crystal (Hitz, Ewing and Hecht, 2012). The non-linear properties of these materials mean that 1064nm photons can cause nonlinear polarization in the crystal. The polarisation oscillates at twice the frequency of the incident photon and in this case radiate a 532nm photon. If diode pumping is utilized then the 532nm emittance can still be high. The most powerful (10-15W output) Nd:YAG lasers employ separate laser heads and power supplies, making them large and immovable (Steiner, 2010). Nevertheless, smaller systems (15cm x 5cm x 30cm (Continuum, 2002)) are now available to integrate into spectrometer systems while still providing 50-200mW power.

PULSING VIA Q-SWITCHING

Further to the excitation source constraints discussed above, an additional requirement associated with performing stand-off Raman spectroscopy is the ability to be able to gate or pulse the laser light in order to create a short burst of high intensity excitation light that will induce a similarly short burst of Raman scatter at the sample. With a short enough burst, the Raman instrument can detect the instantaneous Raman emission without detecting the long lived (and slower) fluorescence emission (Bozlee *et al.*, 2005). Measuring the incoming signal for a short period during this burst also minimises the amount of ambient light detected by the system. One method of creating pulses is known as Q-switching, which works by limiting the stimulated emission within the laser. This is

achieved by placing an attenuator (usually an acousto-optic modulator) within the cavity in order to prevent photons from oscillating and therefore causing stimulated emission. The overall technique is known as decreasing the Q-factor (i.e. the strength of the oscillation damping in the system) (Koechner, 2013). If the pumping rate is faster than the rate of spontaneous emission (the only ongoing emission process while the attenuator is active), there will be a population inversion. Nd: YAG lasers have a slower rate of spontaneous emission compared to gas and ion lasers so Q-switching is far easier to implement. When the population inversion is high enough, the Q-factor of the cavity is increased very quickly (switched) meaning that the light is allowed to oscillate in the cavity for a short period of time (the pulse time is usually a few nanoseconds) (Milonni and Eberly, 2010). With a large population inversion in place, the subsequent short laser emission pulses can be up to 10^9W (Demtröder, 2002). Laser pumping continues throughout operation so there is always a large population inversion when the Q-factor is increased.

Section 2.1.1 of this thesis has outlined the fundamental operation and properties of a range of lasers types, and has reviewed their suitability for both stand-off and in situ Raman spectroscopy. A summary of the most pertinent characteristics for each laser is provided by Table 2.1.

Laser Type	Wavelengths produced (nm)	Power (mW)	Cooling mechanism	Waveform	Life time (hrs)
He-Ne	339 632 151	5-50	Air	Continuous	10 000
Argon	514 488	50-100	water	Continuous	5000
Diode	840 760 1300	5-50	Thermoelectric cooler	Continuous	10 000
Nd:YAG	1064 532	50-200	Water and air cooling	Pulsed or continuous	800

Table 2.1: A summary of the main properties of the lasers discussed in this chapter. Despite having the shortest lifetime the Nd: YAG laser provides pulsed emission at a high power- an essential property for the excitation source for stand-off Raman system.

2.1.2 OUTPUT OPTICS

Laser light must be delivered in an efficient and well defined way to the area of interest on the sample being interrogated. If the path of the laser light is more than a few centimetres, the beam will diverge significantly before it reaches the sample. Consequently, the excitation light is usually delivered to the surface of the sample using a combination of mirrors and lenses. In most cases, the laser light is collimated on exit from the laser cavity (Csele, 2011) because once the light beams are parallel, they can be readily redirected using mirrors. In order to maximise the amount of light reaching the sample, a minimum number of optical elements should be used. To keep the collection optics as efficient as possible, both mirrors and lenses should generate minimum scatter and should be aligned correctly to avoid phenomena such as vignetting. Vignetting,

illustrated in Figure 2.5, occurs when light misses a lens as a result of a lens being too small or a dispersing beam being too large.

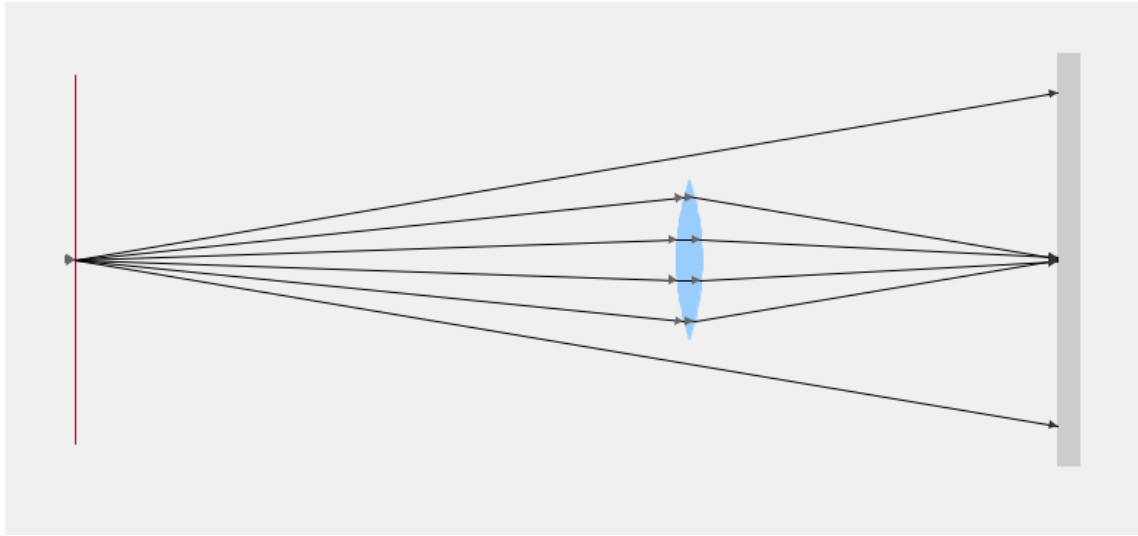


Figure 2.5: A ray diagram illustrating vignetting. The source divergence is such that the two outermost rays miss the lens and therefore not focused (unlike the inner four rays).

Due to the high intensity of the laser beams, precautions have to be taken to ensure that the optics are not damaged. Continuous wave lasers tend to cause damage through thermal effects (the material absorbs the incident radiation). The strong electric fields produced by pulsed lasers however, break down the dielectric structure by stripping electrons from the lattice of a material before causing thermal damage (Wood, 2003). Often, laser redirection mirrors are made from a borosilicate glass or UV fused silica substrate. Materials such as these have well known optical properties and are highly resistant to damage (Webb and Jones, 2004). Schott BK7, the trade name for silicate glass (Cardarelli, 2013), is made primarily of silica, boron oxide, sodium oxide and potassium oxide (Lane, 1990). The mirrors are coated in a highly reflective oxide or fluorides such as PbF_2 , AlF_3 , ZrO_2 , SiO_2 , Al_2O_3 (Basting, 2005). These coatings allow the mirrors to withstand energy fluences of $\sim 8 \text{ J cm}^{-2}$ at 532nm (Thorlabs Inc 2017). A 532nm Nd: YAG laser operating at 35mJ per pulse, with an incident spot size of 2mm, produces a fluence of $\sim 0.3 \text{ J cm}^{-2}$.

Lenses are frequently coated, not only to prevent damage to the optical structure, but also to maximise throughput and minimise back reflection. Ideally, the refractive index of the anti-reflection coating is greater than that of air but less than that of glass; this provides an intermediate double interface between the air and glass. The extra boundary creates extra reflectance, and if the Anti Reflective (AR) coating is the correct thickness, it will

deconstructively interfere with the first reflected wave (Sharma, 2006). The relationship between the AR coating thickness, d , and the wavelength of the light is given by:

$$d = \lambda/4 \quad 2.1$$

where λ is the wavelength of the light.

Materials such as MgF_2 have a refractive index of 1.38. To calculate the percentage of light reflected at each surface, the Fresnel equation is used,

$$R = \frac{n_2 - n_1}{n_2 + n_1} \quad 2.2$$

where, R is the amplitude of the reflected light, n_1 is the refractive index of the secondary medium and n_2 is the refractive index of the initial medium.

This simplified equation assumes an angle of incidence of 0° to the normal. Assuming the glass substrate has a reflective index of 1.8 and the refractive index of air is 1.0, the percentage of light reflected with an AR coating is 2.6% compared with 8.2% of light reflected without a coating. In the case where five lenses are used consecutively (perhaps in a compound optic), coating each lens would increase the throughput of the five lens system by ~22%.

In order to provide enhanced sampling capabilities and instrument mobility/flexibility, the output optics can be remotely coupled to the laser via an optical fibre. For example, Chapter 1 described the potential that stand-off Raman spectroscopy has to enhance a planetary rover's ability to remotely detect material of interest. To do this efficiently, the output optics can be situated on a mast or platform, with the laser system housed in the rover's main body. The two instrument sections may then be coupled via an optical fibre. The details of fibre coupling are described in Section 2.1.4.

The addition of a fibre may also require the inclusion of filters since the laser light will induce a small amount of inelastic scattering (such as Raman) in the emission optics it encounters. Often the excitation light is passed through a filter before it reaches the sample in order to reject additional wavelengths that have been generated as a consequence of scattering effects. The use of filters is discussed in more detail in Section 2.1.3.

Regardless of operating distance, the laser light should be focused onto the sample to ensure a sufficient energy density at the surface. Focusing the source provides a minimum spot (image) size and therefore a maximum energy density. The actual spot size and hence energy density is highly dependent on the sample. For example, crystalline samples will efficiently scatter the incident light, decreasing the energy density experienced by a given molecule. Conversely, if the damage threshold of a given sample is quite low, the maximum energy density achievable by the output optics has the potential to burn and damage the material before the Raman scattering process has occurred (Smith and Dent, 2013). Therefore, a trade-off needs to be performed between spectral intensity and the likelihood of sample damage

Further to this issue, the spot size can influence the spatial resolution at the sample. For example, if the laser spot diameter is small (compared to the grain size or composite variation of the sample), information regarding the heterogeneous nature of the sample could be readily missed. This can be averted by employing a thorough sampling or scanning methodology, which, however, can impact the time required to obtain a sufficient amount of data.

STAND-OFF

The excitation light must reach (and be focused onto) the sample, in some cases, up to 100 metres away. Using adapted versions of the optics described above, the laser light can be delivered to a sample at a remote distance using one of two instrument configurations: oblique and co-axial. A schematic of the co-axial configuration is shown in Figure 2.6. The set-up requires at least two mirrors (in addition to the collimator at the laser exit) to redirect the laser light to the centre of the secondary mirror of the telescope and then to the sample at a significant distance away. Due to the additional mirrors, there will be some loss in laser intensity between the laser cavity and the sample. However, in this configuration the collection optics will not need to be adjusted as the working distance changes (see Figure 2.6)(Sharma, 2007).

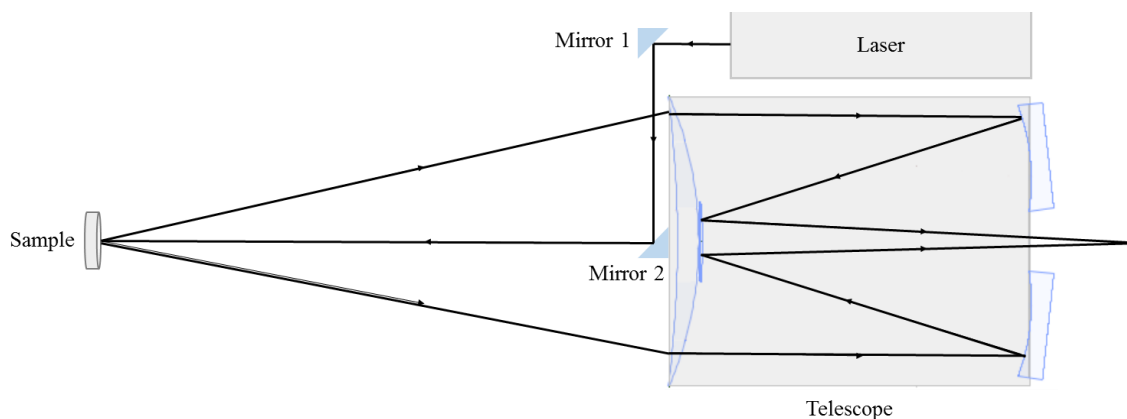


Figure 2.6: A schematic of the co-axial stand-off instrument configuration.

In the oblique configuration (see Figure 2.7), the laser is situated adjacent to the collection optics and the excitation light is focused directly onto the sample. The throughput of this type of configuration is greater than that of the co-axial configuration, since there are no additional mirrors required to redirect the laser light. However, if the distance to the sample changes, the alignment of the collection optics will need to be adjusted (Sharma, 2007).

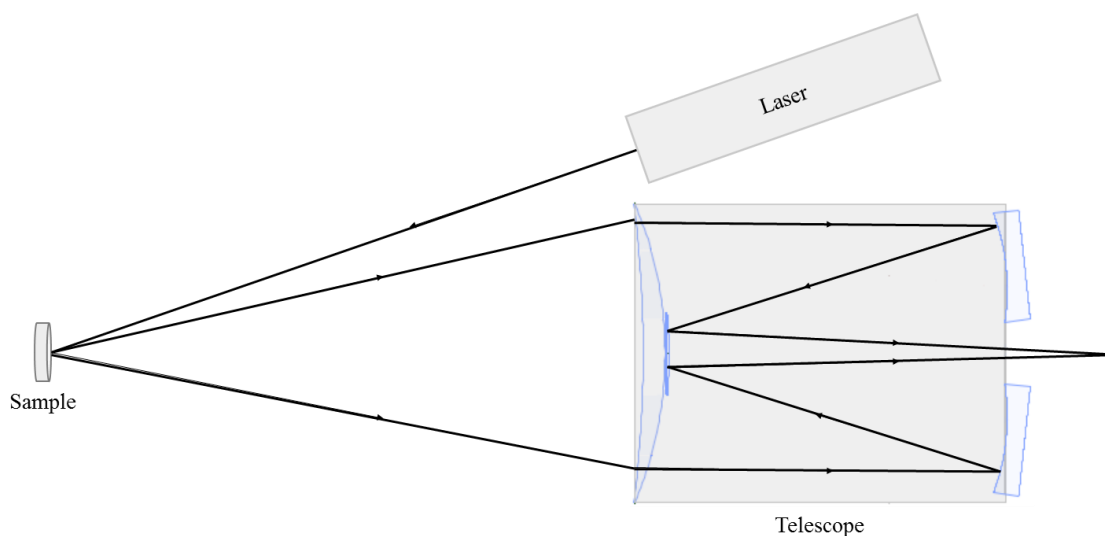


Figure 2.7: A diagram of the oblique configuration often used for stand-off Raman instruments.

The output optical system of a Raman system is responsible for directing the excitation light from its source to a point of interest on the sample. This section described the various ways in which monochromatic laser light is directed onto the sample in a robust and efficient manner. Table 2.2 summarises the advantages and disadvantages of different system geometries and coupling methods.

Configuration	Options	Advantages	Disadvantages
Geometry	Co-axial	- Laser does not need to be refocused if operating distance changes.	- Additional mirrors reduce the efficiency of laser redirection.
	Oblique	- Fewer optics are required to focus the laser onto the sample surface.	- If the working distance of the system changes, the laser would need to be refocused.
Coupling	Optical Fibre	- Output optics (and input-see Section 2.13) can sit apart from the main body of the instrument.	- Throughput losses due to fibre (see Section 2.1.4).
	Direct	- Minimal losses as no extra optical components are required to redirect the laser light.	- Remaining instrument systems such as the spectrometer, laser (and optical head) must be situated close to the spectrometer.

Table 2.2: A table to summarise the options available concerning the system configuration geometry and coupling.

2.1.3 INPUT OPTICS

Input optics are required to maximise the amount of Raman emission collected by the instrument. Fundamentally this is achieved by increasing the size of the initial aperture, which in turn increases the size of the collection cone (see Figure 2.5) (Cheng, 2010). However, in addition to the associated increase in mass, an increase in aperture size will also increase the amount of ambient light and fluorescence light that is collected by the instrument, which may ultimately impact on the signal-to-noise ratio of the obtained spectra.

TELESCOPES

The large distances involved in stand-off Raman spectroscopy require a larger collection aperture (compared to those used in in situ spectroscopy), in order to maintain the overall collection efficiency of the collecting light cone. This relationship is demonstrated in Figure 2.8. Telescopes are often used to achieve this as they are designed to collect a maximum amount of light at a large distance, while still minimising mass and costs. There are three main types of telescope: refractor, reflector and combination; each of which is described below.

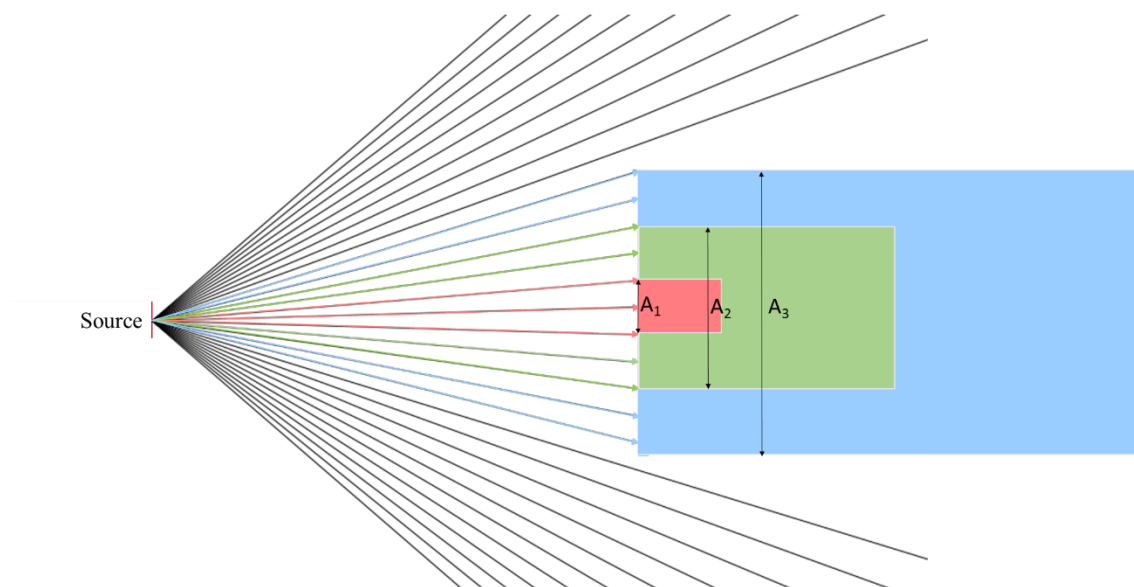


Figure 2.8: An illustration showing the relationship between a telescope aperture, A , and the collection power of the system. The collection power of the system is represented by the number of light rays that intercept with (and are therefore collected by) the telescope.

REFRACTOR

In a refractor telescope, light passes through a large lens (or set of lenses), called an objective lens, at the far end of the telescope tube. An image of a refractor telescope can be found in Figure 2.9. The diameter of this primary lens determines the collection power of the telescope. The light collected by the first lens is concentrated onto a second lens, the eye piece lens. This lens focuses the image formed by the objective lens, so that it can be viewed. This design is relatively simple and rugged making it ideal for use in a robust Raman instrument, but the most powerful refractive telescopes are large and heavy and more costly than the equivalent reflective telescope (to accommodate for the larger lenses and extended focal lengths) (Peston, 2010). The stringent mass and volume requirements of space instrument designs would therefore limit the size and therefore the collection power of a Raman instrument that utilised a refractive telescope.

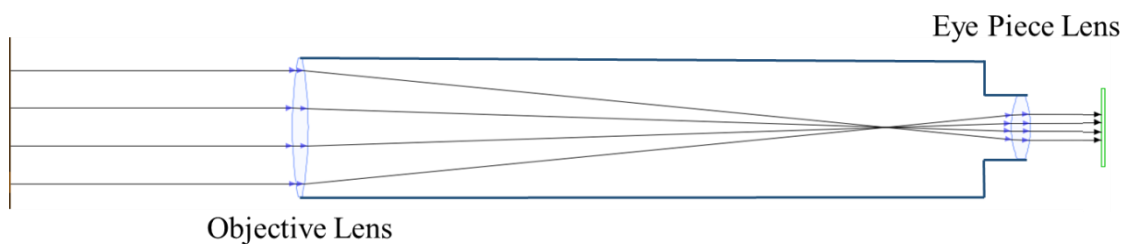


Figure 2.9: Diagram illustrating the optical configuration of a refractor telescope.

REFLECTOR

The reflector telescope was designed in order to overcome the objective size limits exhibited by refractive telescopes. Reflector telescopes use a curved mirror situated at the back of a telescope to focus parallel light rays (light from infinity) back onto a smaller secondary mirror located at the front of the telescope. Light is then reflected into a hole in the telescope body onto a focusing objective (such as an eyepiece). This design is illustrated in Figure 2.10.

Compared to lenses, mirrors are less likely to suffer from optical irregularities causing chromatic aberration. However, light is obstructed by the secondary mirror causing a loss in throughput (typically around 40% of the light collected). This optical set-up allows for much larger apertures since mirrors can be supported from behind, unlike the lenses of a

refractor telescope. Despite a larger aperture, reflector telescopes can achieve a compact, portable and cost effective design (Kitchin, 2013).

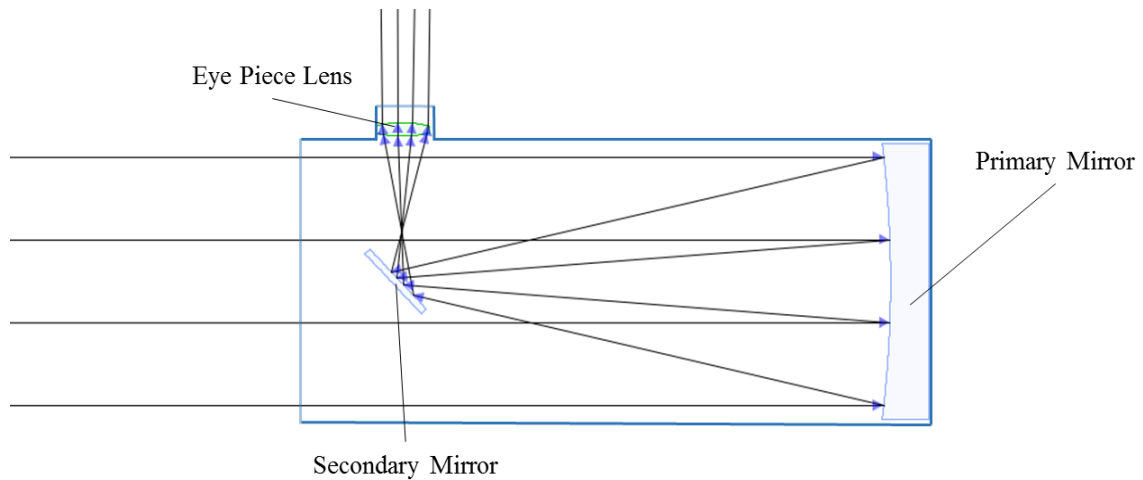


Figure 2.10: A diagram illustrating how a reflective telescope functions.

CATADIOPTRIC (COMBINATION)

Catadioptric telescopes use a combination of curved mirrors (catoptrics) and lenses (dioptrics) to create a more compact design compared to both refractor and reflector telescopes. The most popular designs are Schmidt-Cassegrain and the Maksutov-Cassegrain. These telescopes (and all other Cassegrain telescopes) employ the folded optical path of a standard reflector illustrated in Figure 2. 11. The Schmidt-Cassegrain design uses a Schmidt correction plate (aspherical lens) to correct for aberrations. Maksutov-Cassegrain use a convex correction lens (sometimes called a meniscus lens) on the back of which the secondary mirror is situated at the focal point of the primary mirror (Schroeder, 2012).

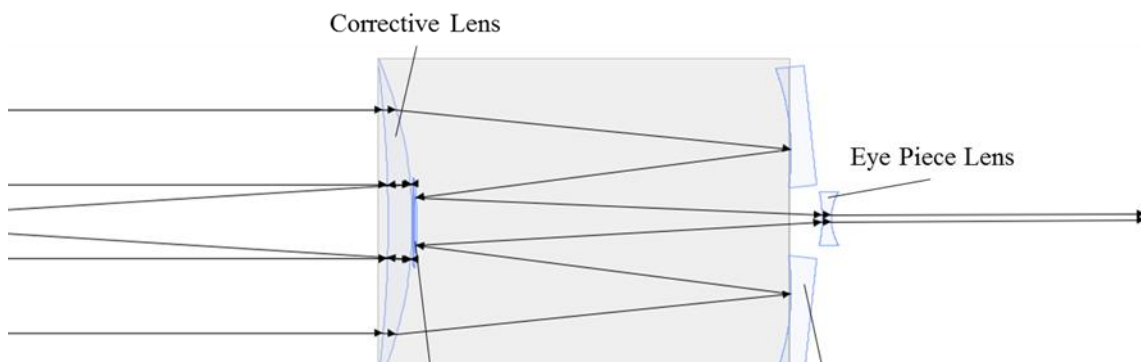


Figure 2. 11: The figure shows the layout of a Catadioptric telescope.

As a result of their complexity, catadioptrics can be expensive compared to reflector and refractor telescopes. However, the optical configuration provides a compact design and a good near focus. The use of correction mirrors improves the quality of the images that they produce. Due to their large aperture sizes, reflector telescopes have been incorporated into stand-off Raman instrument (Angel *et al.*, 2012).

FILTERS

In general, Rayleigh scattering from a sample is 10^6 times stronger than the scattered Raman signal. It is therefore very important to filter out as much of the Rayleigh scattered light as possible that enters the collection optics. Often, a filter can be integrated directly into the collection optics. The most commonly used types are interference filters, which are well developed and understood and are available in several different forms: line, band and cut-off filters.

Interference filters obstruct certain wavelengths by only allowing constructively interfering wavelengths through the material. These filters consist of a stack of 2 types of alternating layers. The two layers are electrical insulators with different refractive indices. The two different indices mean that as light passes through the filter, photons of particular wavelengths are reflected at each surface. Photons with wavelengths equal to a multiple of the thickness multiplied by the refractive index are transmitted at each surface. The transmitted wavelengths constructively interfere and are transmitted with high efficiency (>95%) through the material with little absorption or back reflection. Interference filters are also tuneable by simply changing the angle at which the light is incident on the filter. As this angle is increased, the transmitted or reflected wavelength range also increases (Kawata, 2008).

Figure 2.12 shows the transmission plots of line, band and cut-off filters. Line-rejection filters can obstruct (or transmit in the case of line-pass filters) frequencies with 100 GHz precision. However, large line filters can be expensive compared to other filters. Filters that obstruct a much broader range of wavelengths are called band filters. Band filters (sometimes called notch filters) either obstruct or transmit a selection of wavelengths within a 10nm range of a central wavelength. These types of filters are often used for

Raman spectroscopy since they allow an adapted instrument to detect and measure anti-stokes lines (see Section 1.3.1).

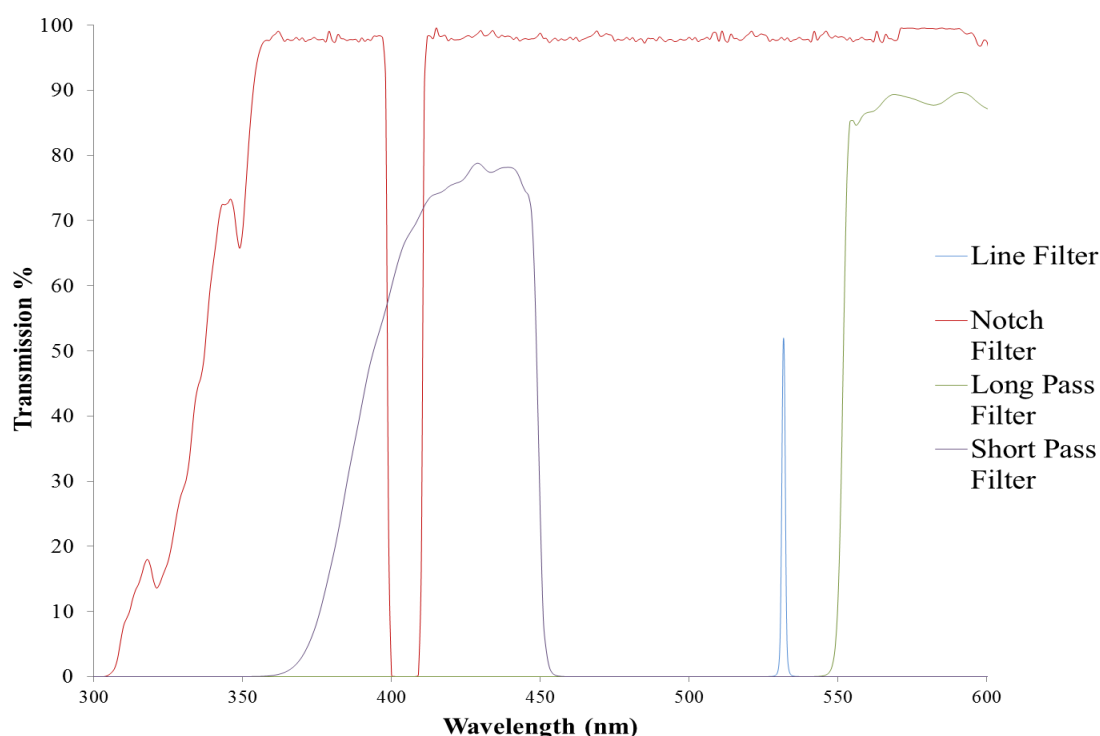


Figure 2.12: A graph showing the transmission efficiency as a function of wavelength for a line pass filter, a notch filter and two cut-off filters; a short pass filter and a long pass filter. The plot was generated using data provided by Thorlabs.

If the instrument design is not concerned with anti-stokes lines then a cut-off filter would be appropriate. Cut-off filters provide a sharp transition from reflection to transmission. For Raman spectroscopy, the cut-off needs to be sharp enough to not obstruct small wavenumber offsets (i.e. $<200\text{cm}^{-1}$). However, the sharper the cut-off, the more expensive the filter. This type of filter would only be appropriate for the detection and measurement of Stokes lines. Interference filters are also not appropriate for high powered pulsed lasers. Similar to lenses and mirrors, filters have specific damage thresholds. Light that is absorbed is diffused as heat and can cause permanent damage to a filter if the level of heat is too high. A typical damage threshold for an interference filter is 25 Wcm^{-2} (when using a CW laser), so they are reasonably well suited for filtering the Rayleigh scattered light produced in most Raman spectroscopy applications.

The input optical system of an instrument collects scattered light emitted by a sample. For a stand-off Raman system, the input optics usually incorporate a telescope to maximise the amount of light collected by the instrument. Table 2.3 summarises the telescopic configurations that could be employed in a stand-off Raman instrumentation. The table also includes reviews the range of filters available to reduce the elastically scattered light collected from the sample.

Component	Options	Advantages	Disadvantages
Telescope	Refractor	- Simple - Robust	- Large in size as they are based on a focal length. - Heavy compared to other designs of equivalent collection power. - Large mass and size makes them expensive.
	Reflector	- Mirrors are less likely to suffer from optical irregularities. - Larger apertures as mirrors are easier to support. - Compact compared to refractor.	- Secondary mirror obstruction.
	Catadioptric	- Compact design even with large aperture. - Lenses to correct for aberrations.	- Secondary mirror obstruction - Complex (lens and mirrors required). - Expensive.
Filters	Line	- High precision transition wavelengths, $\sim 1\text{nm}$. - Allows for anti-stokes measurements.	- Expensive.
	Band	- Allows system to make anti stokes measurements	- Broader transition band ($\sim 10\text{nm}$).
	Cut-off	- Less expensive than a band or line filter.	- Does not allow anti-stokes measurements. - Broader transition band ($\sim 10\text{nm}$)

Table 2.3: A table to summarise the available telescope and filter options.

2.1.4 SYSTEM COUPLING

The collection optics can be coupled to the spectrograph in a number of different ways. The system throughput can be maximised by directly coupling the optics (since there are no extra components to attenuate the light). However, this may not be practical if the movement of the optical head needs to be independent of the spectrograph so coupling is usually achieved through the use of optical fibres.

Optical fibres consist of two materials in a concentric cylinder structure. The material at the centre of the inner cylinder has a low refractive index compared to the material on the outside. As light enters the fibre, it is totally internally reflected off the walls as it progresses along the length of the structure. Small losses in throughput arise from absorption and back reflection from impurities within the glass (core); these losses are wavelength dependent (Bagad, 2009). Connectors, either between fibres or to optics can easily become dirty or dusty and can obscure light, ultimately resulting in significant signal losses. A typical connector will attenuate the signal by less than 0.25 dB (Cvijetic, 2004). A summary of the methods by which the input and output optical systems can be coupled to the spectrograph is provided in Table 2.2.

2.1.5 SPECTROGRAPH

This part of the instrument is used to disperse the collected light into its component wavelengths so that their relative intensities can be measured. The light is initially collimated to redirect the rays onto a diffraction grating or prism at an incident angle of 0° (ensuring that the diffraction of all wavelengths is with respect to the normal). Once diffracted into its component wavelengths, the emerging light is then collected and focused onto a detector located at the focal plane of the spectrograph.

INPUT OPTICS.

The light enters the spectrograph through a slit or entrance aperture, often through a fibre optic as their exit apertures are sufficiently small ($\sim 5\mu\text{m}$). The entrance slit controls the angle at which light enters (Zou and Hutton, 2011). For this reason, it partially determines the resolution of the spectrograph. The smaller the slit, the more spatially confined the incident light is. However, a smaller aperture allows less light to enter the spectrograph so overall throughput is compromised.

Once the light enters the spectrograph it is collimated (directed into parallel beams) by a lens or multiple lenses. It is important to optimise the collimation since the diffraction grating will spatially split the incoming beam by redirecting a photon to an angle (from the beam plane) proportional to its wavelength (this process is described later in this section). Incoming photons should therefore arrive at the grating at an identical angle so each wavelength can be angularly separated relative to the incoming beam.

As described previously (in Section 2.1.2) there are many important factors (such as vignetting and coating damage) that can affect the throughput and collimating power of the input optics. All optical components have a diffraction limit that prevents perfect collimation. The performance of a collimator can be described through point spread functions (a measure of the amount of spreading). Often multiple lenses (or combination lenses) are used to reduce vignetting and resolution loss but will in turn reduce throughput compared to a system based on a single lens.

DIFFRACTION GRATING

The diffraction grating disperses the incoming beam into its component wavelengths. There are two types of grating: ruled and holographic. A ruled grating consists of many small grooves. As incident light exits the grating it is diffracted, to an angle, θ , proportional to its wavelength as shown in Figure 2.13. Ruled and holographic gratings can also be reflective (the angle of reflection depends on the wavelength of the incident light) or transmissive (incident light is transmitted through the grating substrate but the exit angle, with respect to the angle of incidence, depends on the wavelength of incident light).

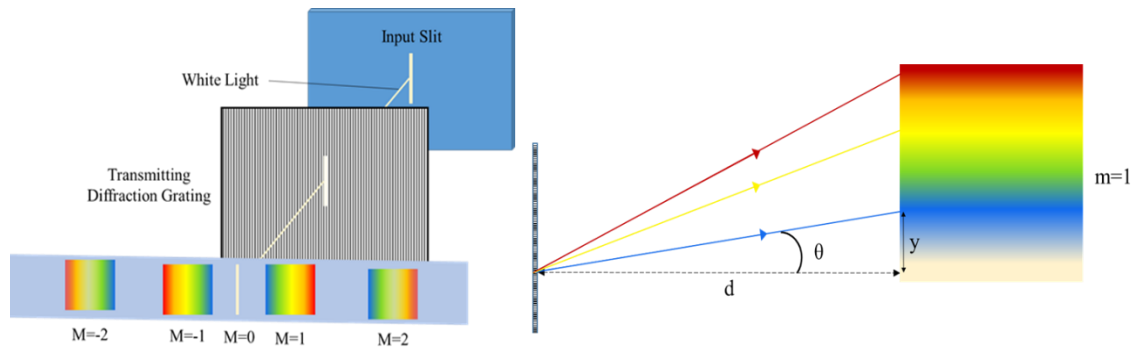


Figure 2.13: A diagram showing the array of diffraction orders produced by light incident on a grating (left) and the relationship between the angle of diffraction and the wavelength of the incident light (right).

The performance of a diffraction grating depends on several properties including its size, groove frequency and blaze angle. The characteristics of a grating can have a large impact on the resolution, spectral range and throughput of the system. For example, (and as with the other optical components) the grating must be large enough to avoid the effects of vignetting. However, larger gratings are more expensive to manufacture. Equation 2.3 illustrates how the spectral range of the spectrometer is dependent on the groove density of the grating,

$$\sin \theta = \frac{m\lambda}{d} \quad 2.3$$

where θ is the angle of diffraction, m is the diffraction order (see Figure 2.13), λ is the wavelength of diffracted light and d is the separation distance between slits in the grating. The more grooves a grating contains, the larger the diffraction angle of a given wavelength. Equation 2.3 also implies that the wavelength per unit distance will decrease,

improving the resolution. However, there are geometric limits on the spectral range that result from the finite size of the lenses and detectors. This highlights an important trade-off between fitting a large spectral range onto a detector and maximising the spectral resolution.

Holographic gratings are created by two incident UV lasers, which, when combined, engrave a sinusoidal interference pattern on the surface of glass. This manufacturing process achieves a higher number of grooves per mm compared to a ruled grating (<6000 grooves/mm) (Schrenk, 2012). This method gives a much more uniform response across the grating but suffers from transmission efficiencies which can be as low as 60%. These gratings can also be formed on concave surfaces, enabling them to act as a focusing and dispersive component simultaneously.

To increase the throughput of a particular diffraction order, $m = -1$ for example, ruled gratings are often blazed. Blazing adds a small prism onto each groove of the grating. As illustrated in Figure 2.14, the angle of the prism (the blaze angle) is added onto the original angle of refraction, but only in one particular direction. Incident light is then refracted more in the direction of the blaze angle compared to the other side of the normal ($m=0$). The additional light refracted in that direction makes one order ($+1$) brighter compared to the equivalent on the opposite side of the normal (-1) (Hobbs, 2013).

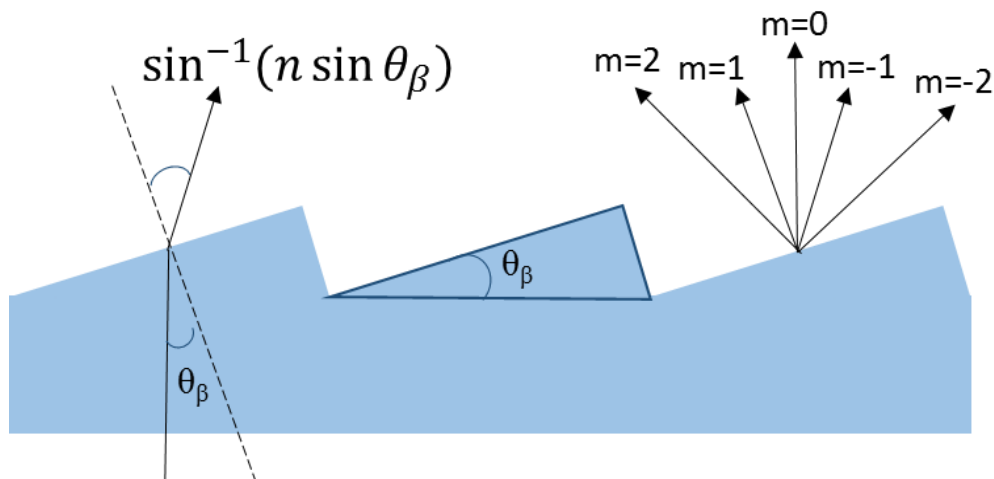


Figure 2.14: A diagram illustrating the effects of a blazed grating. The additional prism redirects the incoming beams to angle equal to that of the $m=-1$ order.

OUTPUT OPTICS

The output optics focus the diffracted light onto the plane of the detector. Again, vignetting can be an issue if the lens is not sufficiently large enough to focus all of the

incoming light. In this case, the edges of the diffraction order may be lost from the overall signal. Aberrations can also cause losses in throughput, but can normally be corrected by using a combination of lenses. Using a changeable combination lens enables the focal length to be modified, and therefore the size of the image. This can be beneficial if the spectral resolution needs to be maximised within a particular section of the spectral order.

The instrument spectrometer spatially separates the collected light into its component wavelengths so that the relative photon intensities can be measured. Usually the incoming beam is separated using a diffraction grating. The advantages and disadvantages of different grating types are summarised in Table 2.4.

Component	Options	Advantages	Disadvantages
Diffraction Grating	Ruled	- High transmission efficiency. - Can be blazed to increase the intensity of a particular diffraction order.	- Less expensive as they are easily made in comparison to holographic gratings. - Limited grooves/mm due to manufacturing process.
	Holographic	- High number of grooves/mm. - More uniform response across the grating. - Can be manufactured onto focusing optics.	- Expensive due to manufacturing process. - Comparatively low throughput.

Table 2.4: A table comparing the characteristics of ruled and holographic gratings.

2.2 DETECTORS

In order to efficiently and accurately measure as much of the Raman signal as possible, stringent requirements are placed on the performance of the detection system. For example, the size of the detector should be sufficient to detect the diffraction order focused by the spectrograph and with adequate resolution (see Section 2.1.5 for more detail). The detector must also be sensitive to specific wavelengths, i.e. the detector must efficiently detect photons with wavelengths in the range of 533-650nm, for example, to measure Raman bands with wavenumbers of 20-2000cm⁻¹, excited using a 532nm laser. There may also be requirements placed on the data acquisition time scales, depending on the Analogue to Digital Conversion (ADC) sampling process. For example, if an instrument is to be used in the field as opposed to in the lab, it may be necessary to obtain spectra on a shorter time scale due resources and difficult environmental conditions. Detectors used on moving spacecraft also have strict data acquisition requirements. When considering stand-off spectroscopy, the fast acquisition of a Charge Coupled Device (CCD) image (containing a Raman spectrum) is not necessarily needed but by collecting light emitted from the sample for a very short time, the system is able to avoid the delayed fluorescence emission (see Chapter 1, section 1.3.1). Usually the image rate of a stand-off instrument is driven by other factors such as a specific detector operating mode, instrument sampling rates (i.e. the length of time for the total experiment) and the time until the sample is damaged by the incident laser. In light of these detector requirements, this section focuses on the different sensors available and the operation modes that could be employed to efficiently detect Raman emission especially from a significant distance.

2.2.1 CHARGE COUPLED DEVICES (CCD)

Charge coupled devices were first developed in 1969 (Boyle & Smith 1970) as a method of collecting and measuring photons. They typically consist of a fabricated silicon p-n junction, on top of which is a silicon-dioxide insulating layer (Zou and Hutton, 2011). Above this layer is a repeating network of 2, 3 or 4 electrodes (or gates). The gates are arranged in a grid over the device, with columns of gates insulated from each other (by structures known as channel stops). A singular set of (2, 3 or 4) electrodes and a channel stop defines a region in the device known as a CCD image pixel. By grounding the bottom

layer of the silicon substrate (the p-type layer) and applying a positive voltage to the upper, n-type layer (via the electrodes), the depletion layer in the p-n junction is extended (see illustration in Figure 2.15)(Janesick, 2001). Charge is predominantly created in this layer via the photoelectric effect (although it can also be generated in neighbouring layers). Photons with sufficient energy will promote electrons from the valance energy band into the conduction energy band, creating an electron-hole pair in the substrate (i.e. 1.14eV, which is the bandgap energy of silicon)(Strehlow and Cook, 1973). The resulting electron is then drawn to the n-type material by the positive electrode. The charge is held within a defined region in the silicon (in a pixel) by the potential difference across the substrate. The charge is prevented from entering neighbouring fields by the channel stops and the high potential generated by the other gates in the pixel. The number of electrons within a pixel increases as a function of time until the pixel becomes full or the device is read out.

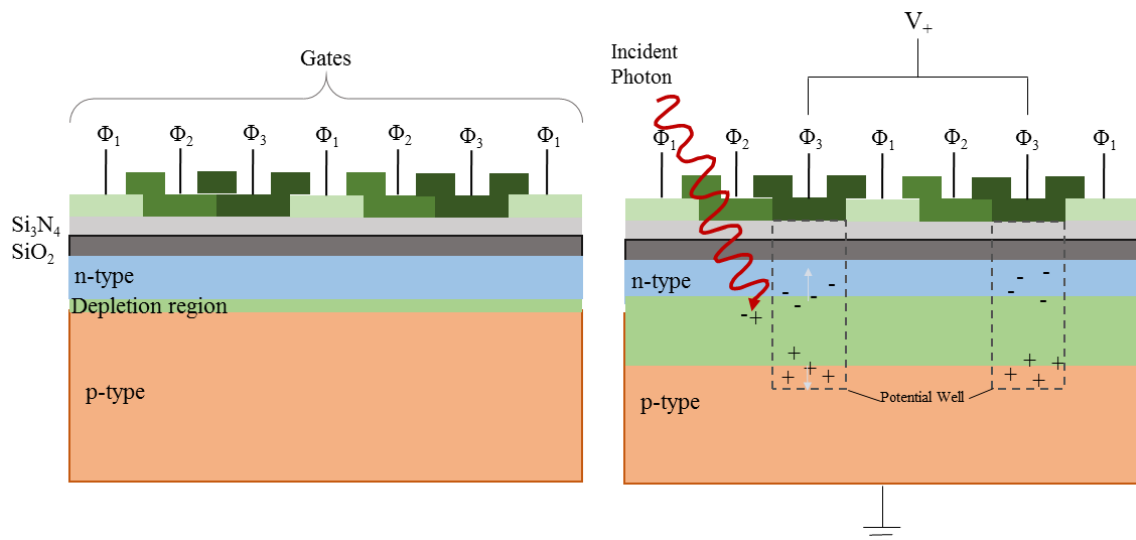


Figure 2.15: A simplified diagram of the internal structure of a CCD. The n-type layer is often silicon doped with phosphorus to create a region with a large concentration of mobile electrons. Similarly, the p-type semiconductor layer consists of silicon doped with boron and exhibits a large concentration of holes.

The number of electrons that a pixel can hold is referred to as the full-well capacity. The well capacity of a given detector depends on a number of parameters: the pixel size, the type of silicon wafer (i.e. the purity and the quantity of doping in the material) and the architecture of the particular type of CCD. For example, a back illuminated CCD47–20 has a well capacity of 1×10^5 electrons (e2v Technologies, 2011) while a back illuminated CCD30-11 pixel typically holds 5×10^5 electrons (e2v Technologies 2016). It is also important that the depleted region occupies as much of the silicon depth as possible. The

silicon will then not only have a larger capacity for holding electrons, but since it is naturally devoid of electrons, charge found in this region is likely to be from a photon interaction (Janesick, 2001).

Before the charge cloud diffuses away, the charge is moved across and out of the device by manipulating the gate voltages. As the charge accumulates inside a pixel, one gate is held at a high voltage (around 10-12V) creating a potential well to store the electron cloud, as shown in Figure 2.16(a). The other two gates are kept at 0V to prevent charge from moving into vertically adjacent pixels. Charge is also prevented from moving into another column by channel stops (Zou and Hutton, 2011). Once integration is complete, the charge is moved (vertically) to an adjacent pixel by setting the voltage on the second electrode to high, as shown in Figure 2.16(b). The overlapping potential wells extend the electric field and the charge spreads out under both electrodes. The voltage on the initial gate is then removed, completely shifting the charge into the second potential well, as illustrated in Figure 2.16(c).

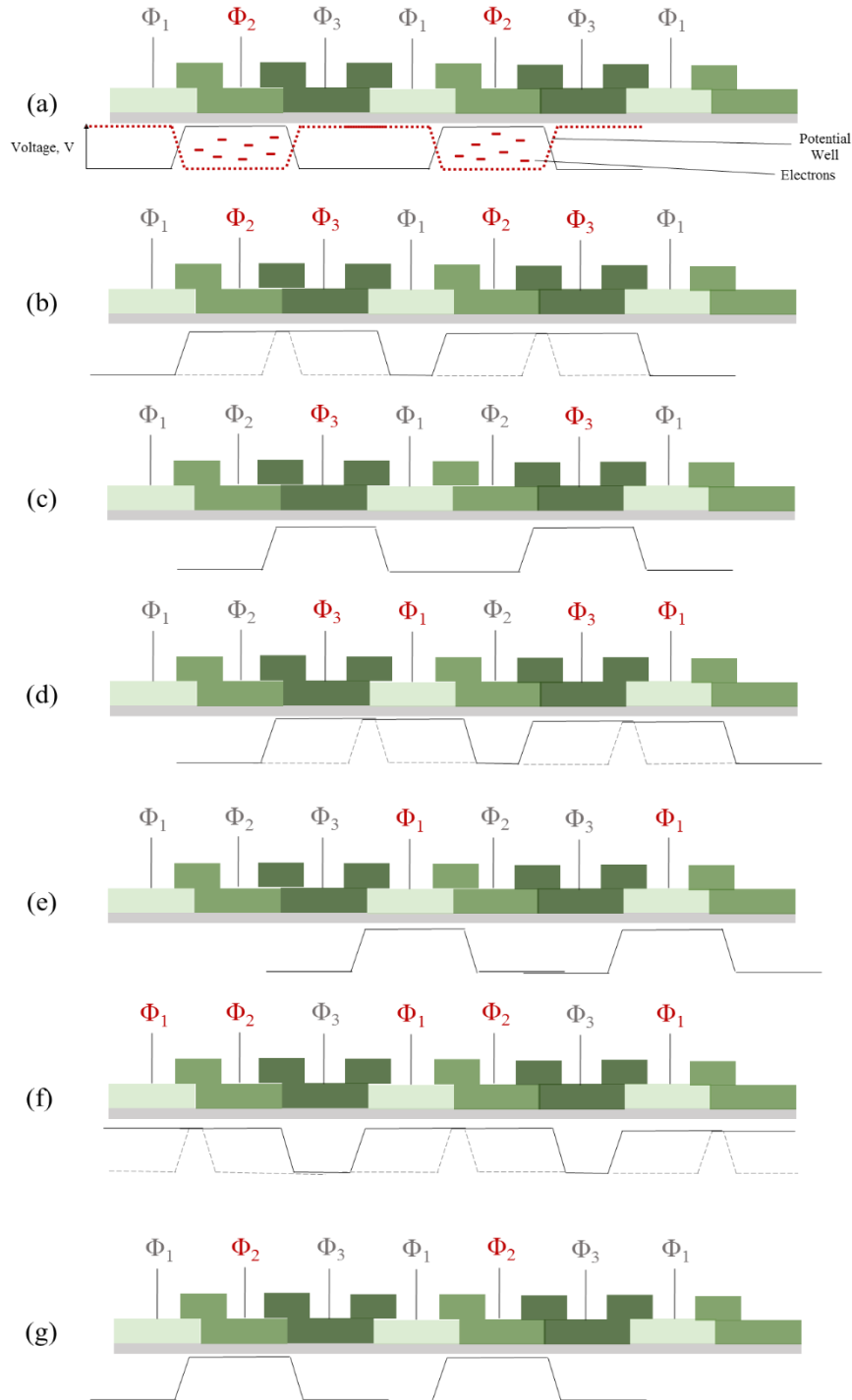


Figure 2.16: A diagram illustrating the sequence of the gate voltages that shift charge from one pixel to another (vertically though the device). The first illustration (a) shows how the electrons are stored within the potential well generated by the gate voltage.

Charge is then moved to another well created by a 3rd electrode and then again into the 1st potential well of the adjacent pixel. Some devices such as the CCD230-42 require a 4th electrode to completely move the charge from one pixel to another (e2v technologies,

2003a). Other devices move charge using only two gates. The gate sequence described here (and illustrated by Figure 2.16) is referred to as a parallel register; charge in all of the pixels, in a given row, is shifted to the rows below simultaneously.

At the bottom of the device resides a serial register, which encompasses an analogous set of gates to the parallel registers. When sequenced in a pattern similar to that described above, the serial gates shift the charge in a single row out of the device onto the output nodes. Each pixel in the serial register however can hold up to five times more charge than a pixel in the image region of the device. This aids processes such as vertical on-chip binning: the movement of charge from multiple rows into the serial registers to increase the measured signal and to decrease the relative impact of noise (discussed in the next part of section 2.2.1).

Once a row (or multiple rows) of charge have been shifted into the serial register, the charge is passed, pixel by pixel, towards the output gate, OG, via the summing well. The summing well is an additional pixel that, like the serial register pixels, is capable of containing charge from multiple pixels. Because of this, the summing well can be used for the horizontal binning of pixels (Janesick, 2001). The OG is held at a low voltage ($\sim 3\text{V}$) to stop charge flowing back into the serial register or forward onto the sense node (capacitor) (Aschenbach *et al.*, 2000). The gate could also be held at a high voltage if it is required to handle a binned packet of charge within the summing well (Janesick, 2001). From the output gate, the charge is then shifted to the sense node, illustrated in Figure 2.17. The sense node incorporates various inter-node capacitances, which are specific to a particular device. The sense node capacitance is reset (charged) to a known level using the Reset Drain (RD, usually at $\sim 17\text{V}$) using a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) (Foy, Foy and North Atlantic Treaty Organization. Public Diplomacy Division., 2005). The gate of the MOSFET is connected to the reset clock (or gate) (Φ_R), the drain is connected to the RD voltage level and the source is connected to the sense capacitor. When the reset clock voltage increases, the MOSFET acts as a switch to charge the capacitor. Due to the capacitive coupling through the MOSFET and the large voltages used, the reset pulse alters the waveform of the charging capacitor, i.e. the reset pulse can increase the charge on the capacitor beyond the desired reset level. As the reset pulse decays, the capacitor also decays to the required reset level (Janesick, 2001). The electrons on the sense node will induce a voltage across the capacitor proportional to the magnitude of the charge (as shown by Equation 2.4),

$$V = \frac{Q}{C} \quad 2.4$$

where V is the induced voltage, Q is the charge transferred in coulombs and C is the capacitance of the sense node in Farads. Typical output node capacitances are usually in the range 0.1-0.05pF. The induced voltage is then connected to the on-chip amplifier. This amplifier is a Field Effect Transistor, in a “source follower” configuration. The gate of the source follower is connected to the sense node. The transistor drain is connected to the output drain, OD (which is held at a voltage of around 30V) and the source is the Output Source (OS) of the CCD. In this configuration, a current flows between the drain and source, with the source held at a particular voltage as a result of a current flow through a load resistor (configured in parallel to OS). The voltage at the transistor gate (which is proportional to the charge on the sense node) will be multiplied by an amplification factor (due to the load resistor in the configuration; see below) and added to OS base voltage. The potential difference between OD and OS is usually around 6V (OS has a base voltage of 24V which is the optimum operating voltage for the FET).

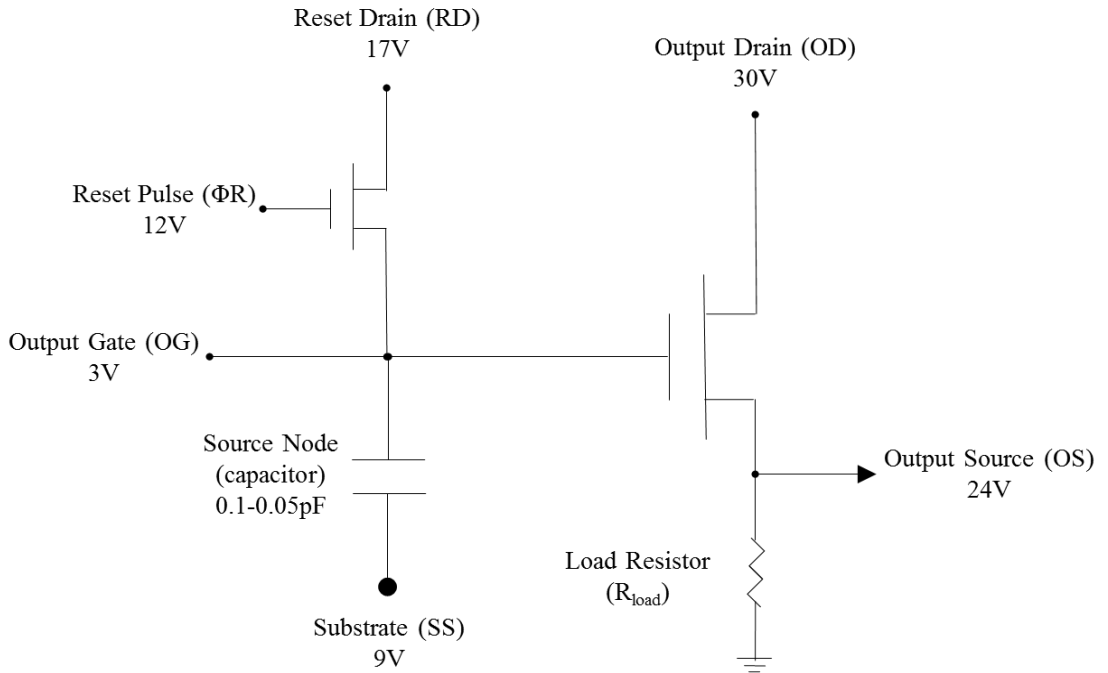


Figure 2.17: A diagram of an integrated CCD circuit. In its simplest form, the circuit consists of two MOSFETs, a capacitor and resistor. Approximate voltages are given for each of the set biases.

The integration of a load resistor, R_L , in this configuration also provides an amplification to the system. The gain (given by Equation 2.5) is less than 1 and depends on the size of R_{load} and the transconductance, g , of the FET,

$$\frac{V_{out}}{V_{in}} = \frac{R_{load}g}{1+R_{load}g} \quad 2.5$$

The combination of the capacitance and the transistor gain (amplifier) results in a CCD sensitivity or responsivity, which gives the number of volts output per accumulated electron, usually in the range of 2-8 μ V per electron.

If a variable responsivity is required (maybe for X-ray detection) then OD can be raised to a higher voltage to handle more charge (due to binning of multiple pixels into the summing well). The resulting analogue signal from the output source is usually amplified again and digitised using an external Analogue to Digital Converter (ADC). This process (and its optimisation) is discussed in next part of section 2.2.1.

The time taken to read out a CCD and obtain an image is variable, as it depends on many factors including the number of pixels that are being clocked out, the frequency of the clocking (i.e. the number of pixels read out per second) and is proportional to the read noise (Hopkinson and Lumb, 1982)(as discussed in the next part of section 2.2.1). It can however be optimised for a given CCD structure and particular operating modes.

CCDs are available in many forms and sizes. The smallest form is a linear or line sensor (Waltham, 2013). These devices contain a single row of pixels (as illustrated by Figure 2.18(a) and can be quickly read out (as parallel clocking of charge is not necessary), while the image is scanned across the surface of the CCD. With a relatively lower number of pixels to read out, the speed of data acquisition is maximised. However, it is then necessary to focus all of the light into a single row of pixels, which limits the dynamic range that can be achieved (the full well capacity divided by the noise).

Alternatively, all devices are available in the form of full frame detectors. Figure 2.18(b) shows a diagram of a full frame CCD. An image is focused and integrated onto an array of pixels and then each is read out in turn, similar to the method described above. An example of this is the CCD42-10 manufactured by e2v (e2v Technologies, 2016). Compared to the linear devices, these allow for operation modes such as binning and, because there are more pixels, more light can be collected without having to sacrifice dynamic range.

CCD detectors are also available in the frame transfer configuration. In this form, a device is divided into two sections (see Figure 2.18(c)). The top section is the image area. Once integrated, charge is clocked rapidly downwards into the bottom, optically shielded half. The charge in the shielded region is then clocked out slowly through the serial register while incoming light continues to generate charge in the image area. An example of such a device is e2v's CCD47-20 (e2v Technologies, 2011).

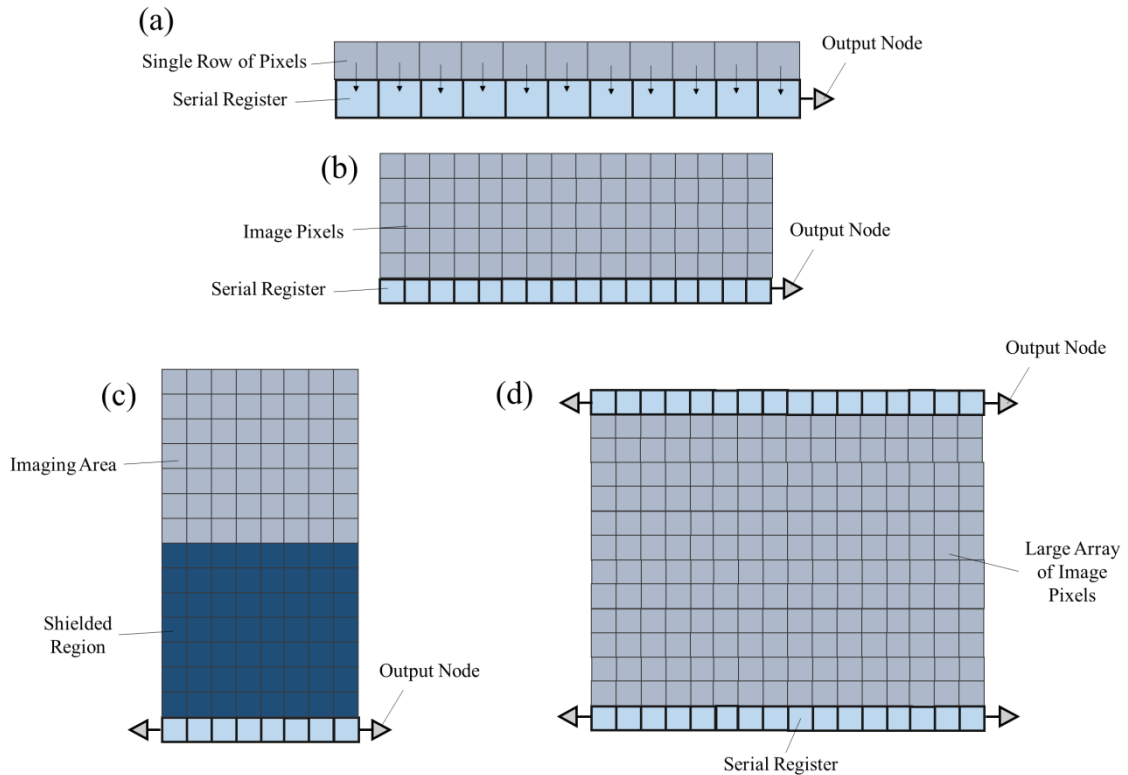


Figure 2.18: Diagrams to illustrate a selection of different CCD structures. Diagram (a) depicts the structure of a line or linear CCD. Image (b) shows a diagram of a full frame device, (c) shows the structure of a full frame device and (d) shows a large CCD that utilises multiple output nodes.

In some cases a full frame device is split into 2, 4 or more regions, allowing for split (and therefore faster) frame transfer. In this configuration there are 2 or 4 different sets of image clocks and two read-out registers. Each half of the full frame device is clocked vertically towards a serial register and then each quadrant is clocked horizontally towards different output nodes. Two of the quadrants (one half of the device) could, for example, act as a storage area. These devices, such as the CCD230-42, have 4 output amplifiers (which increase the rate of data acquisition compared to a standard full frame or frame transfer device)(e2v technologies, 2003a). However, increasing the number of output nodes increases the complexity of the associated electronics and data processing

algorithms. A simplified schematic of a CCD with multiple output nodes is shown in Figure 2.18(d).

In order to speed up the data acquisition time of a device, windowing around specific rows can be implemented. While a device is windowing, a number of the device rows, which do not contain spectral information, are clocked rapidly through the device into the serial register. However, the serial gates typically clock the charge into the dump drain. At this point, charge integrated from the spectral order is at the bottom of the device, ready to be readout slowly into the output node. Once the rows containing spectral information have been clocked out, the remaining rows are rapidly discarded (dumped).

Another operating mode commonly utilised when integrating dynamic signal (such as a moving image) is time-delayed integration (TDI). During TDI operation, a device is continuously exposed to a moving light source. If newly generated charge is then shifted through the device at a rate identical to that of the moving source (and in the same direction), then the source photons will always contribute to the same localised collection of photoelectrons in the device (Van Altena, 2013). This method is often employed on orbiting spacecraft imagers, so that the charge can be integrated over a long time (increasing the detected signal) compared to several quick snap shots of an image as it moves past the surface of the detector (Waltham, 2013). TDI also negates the need for mechanical or electrical shutters, which can cause reliability issues when deploying camera systems in space.

In terms of spectroscopy, it would be possible to implement a similar technique to acquire many images of a thin diffraction order on one device. For example, Figure 2.19 shows a diffraction order containing a Raman signal incident on a small fraction of a CCD. After a short integration period, the charge resulting from the order is shifted down to another (preferably shielded) subsection of the device, leaving the fraction above clear to integrate the diffraction order again. If the incident Raman signal was sufficiently intense (perhaps through using a pulsed laser), all signals, including unwanted ambient light, would be integrated for a short period of time. Compared to the intense Raman signal, the amount of ambient light integrated by the detector would be small. This operation mode would be highly beneficial to systems operating in daylight conditions without a mechanical detector shutter.

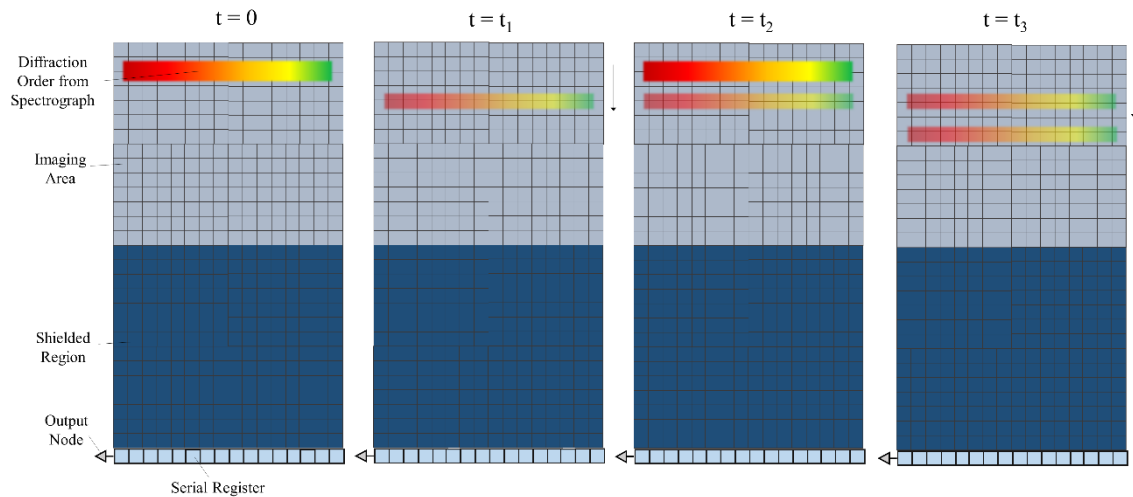


Figure 2.19: An illustration of a pulse integration operating mode using a frame transfer device. At $t=0$, a small amount of signal (i.e. the signal generated by a few 5ns laser pulses) is integrated onto the device. At $t=t_1$, the integrated charge is shifted towards the serial region, away from the region where the pulse were initially incident. At time t_2 , the device integrates an additional set of pulses and these are too shifted towards the serial region. The process continues until a sufficient amount of data has been collected.

A particularly important property of a CCD is the Quantum Efficiency (QE). QE is the efficiency with which photons are converted to electrons within the device and is a function of photon wavelength. The QE of a CCD can be optimised in a number of different ways, such as by applying an anti-reflection coating (see Section 2.1.2) to the front of the CCD package. QE can also be improved by implementing an alternative structure to that illustrated in Figure 2.15. CCDs are typically available in both front and back illuminated formats. Figure 2.15 shows a front illuminated device. In this configuration, incoming photons must penetrate the device gate structures to reach the light sensitive region of the silicon where they can be collected. Incoming light is

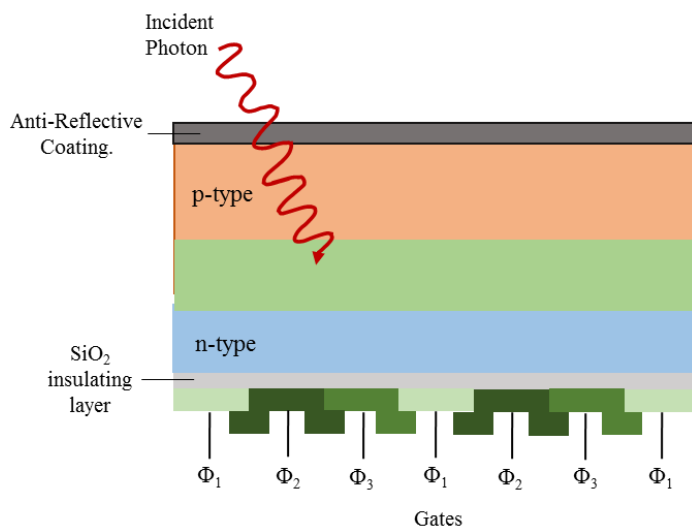


Figure 2.20: A diagram depicting the cross section of a back illuminated CCD.

therefore obstructed or absorbed by the dead layer, resulting in a QE of around 50% in the visible region for front illuminated devices.

To improve detection efficiency, devices can be illuminated from the back, as illustrated in Figure 2.20. In this case, the bulk silicon needs to be mechanically or chemically thinned in order to allow light to penetrate into the photosensitive region. In these devices, the electrode structure is located behind the substrate. Anti-reflection coatings can also reduce losses (see discussion Section 2.1.2). A typical QE for a back illuminated device is ~95% over the visible range (e2v Technologies, 2016). In addition to this the photosensitive region can be made thicker, making it more sensitive to longer wavelength photons (which travel further through the silicon before being absorbed compared to shorter UV wavelengths). However, back illuminated devices suffer from etaloning (often referred to as fringing) (Liang, 2013); a constructive and deconstructive interference pattern caused by the interaction of coherent photons on the surface of the device. Back-illuminated devices have a tendency to generate etaloning, in comparison to front illuminated devices. This is particularly prominent in the NIR wavelength range and can

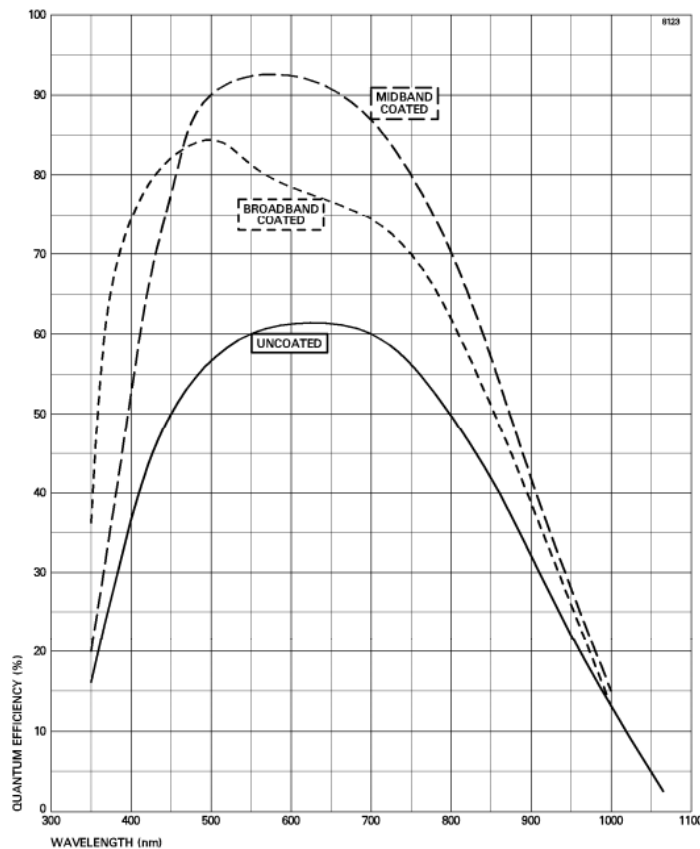


Figure 2.21: A plot of the quantum efficiency of a CCD47-20 back illuminated device taken from (e2v Technologies, 2011). The plot shows the QE of an uncoated device, as well as two devices coated with anti-reflection material.

reduce the measured signal up to 40% (Andor, 2016). This is not the case with front illuminated devices since longer wavelength photons do not interfere.

SOURCES OF NOISE

There are several sources of noise in a CCD based camera systems that degrade the signal measurement process. Each of these sources is discussed in detail in this section.

Reset noise

Reset noise is a result of thermal energy fluctuations within the sense capacitor. The fluctuations, known as Johnson noise (Johnson, 1928), lead to a level of uncertainty in the level at which the capacitor is reset and thus uncertainty in the level of charge subsequently shifted onto the node (hence the name ‘reset noise’). The Johnson noise (in volts), for the reset channel is given by

$$v = \sqrt{4kTBR} \quad 2.6$$

where T is temperature, k is Boltzmann’s constant, B is bandwidth (the range of frequencies over which charge is transferring onto the capacitor) and R is the resistance of the FET. The bandwidth is given by

$$B = \frac{1}{4RC} \quad 2.7$$

where C is the capacitance of the sense node (Hopkinson and Lumb, 1982).

The effects of reset noise can be reduced using Correlated Double Sampling (see discussion in given in the Sampling and Digitisation subsection below).

On-chip amplifier (FET noise)

There are two types of noise that dominate within the on-chip amplifier. The first is flicker noise (also known as $1/f$ or pink noise). Flicker noise is inherent in all electronic devices and thought to originate from the unwanted mobile charge in the component (Janesick, 2001), i.e. the interactions between charge and traps within the silicon oxide interface of the FET. Flicker noise decreases with increased bandwidth (exhibiting a $1/f$ relationship)

as illustrated in Figure 2.22. If charge is moved through the FET at a greater speed, electrons will have a lower probability of becoming absorbed and then released by the traps (which have specific capture and release time constants). The variation of flicker noise with frequency is given by

$$Noise_{flicker} = \sqrt{1 + \frac{f_c}{f}} \quad 2.8$$

where f_c is the corner frequency (The corner frequency is the frequency at which the flicker noise no longer dominates over the white noise) and f is the frequency of readout operation.

The second form of noise that is present in a FET is white noise. White noise arises from fluctuations caused by thermally excited electrons within the imperfect structure of the FET (similar to the reset noise) and is constant with respect to operation frequency (Janesick, 2001).

Pre-Amplifier

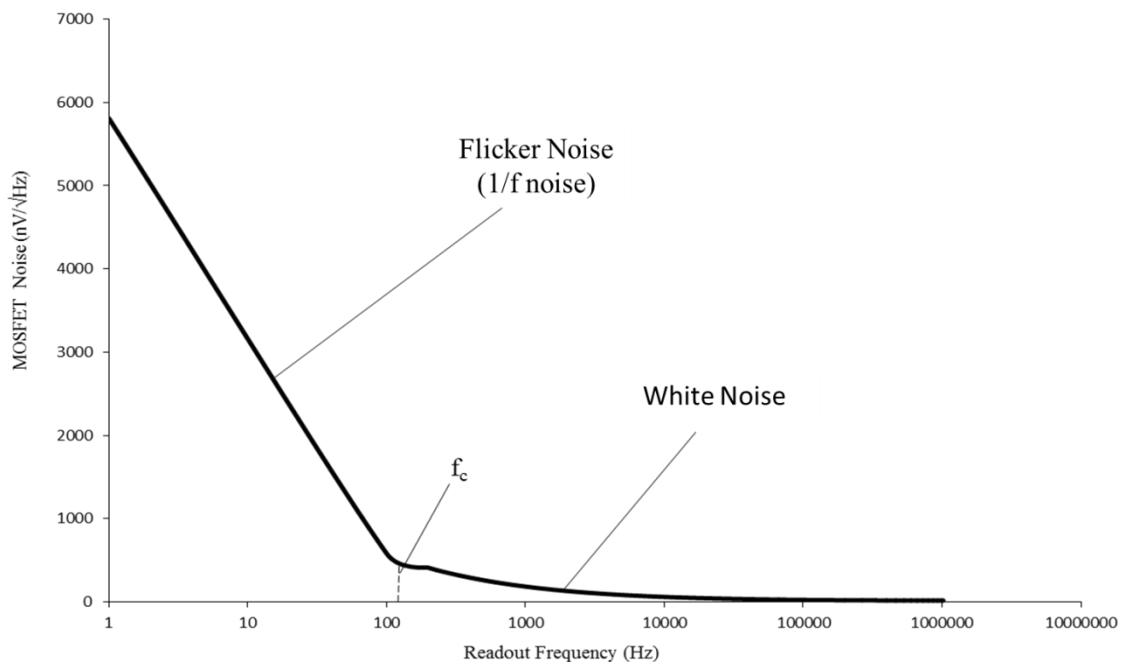


Figure 2.22: At smaller bandwidths, flicker noise is the most predominant source of noise and at larger bandwidths, white noise will dominate. The point at which one begins to dominate over the other depends on the FET properties.

Often the CCD signal is amplified by using an external operational amplifier. This amplifier adds a small amount of noise to the end-to-end system performance. The typical

input referred noise for such an amplifier is $1.7\text{nV}/\sqrt{\text{Hz}}$. So for a system with a 1MHz bandwidth and detector with a responsivity of $2.5\mu\text{V}/\text{e}^-$ the amplifier contributes around 3 electrons.

Sampling and Digitisation

Another important aspect of the readout sequence is the procedure for sampling the output signal of the CCD. This process and its bandwidth limiting properties must be well understood and optimised as it introduces a significant impact on the read noise of the detector system. This section outlines the various factors that affect the overall system read noise and describes one of many sampling techniques known as correlated double sampling (CDS). CDS is the process of sampling a pixel's signal twice; once after the reset level (after the reset pulse feedthrough) and once after the pixel charge has been added to the signal (see Figure 2.23).

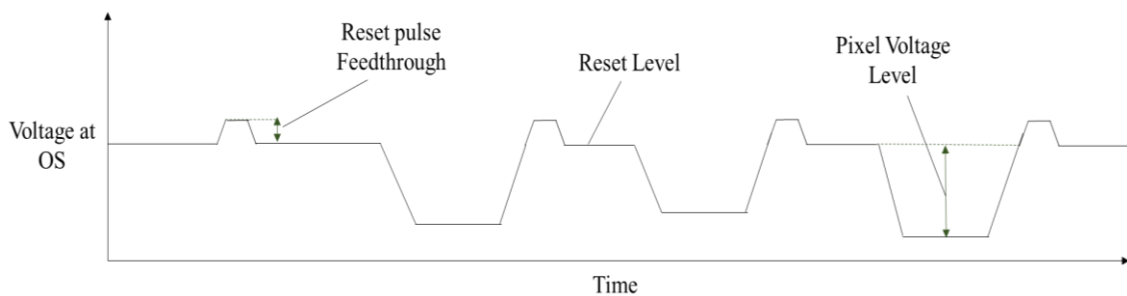


Figure 2.23: A timing diagram to illustrate the points at which the CCD output is sampled during the CDS process.

The amplitudes of these two samples are then differenced using an operational amplifier and the resulting signal is digitised. This subtraction process significantly reduces the effect of the uncertainty in the reset level.

The CDS is also used to reduce low frequency noise and can be performed in a number of different ways (i.e. different sampling schemes can be used). To optimise the system, a scheme is usually chosen depending on the characteristic noise spectrum and the system requirements, such as speed and power consumption.

Each scheme exhibits a particular response function that determines the frequencies that will be sampled efficiently by the system and those that will not. An optimum sampling

scheme would attenuate low frequency signals but sample frequencies that match the CCD readout speed. An example of a double delta sampling response function (at a sampling rate of 200 KHz) is shown in Figure 2.24.

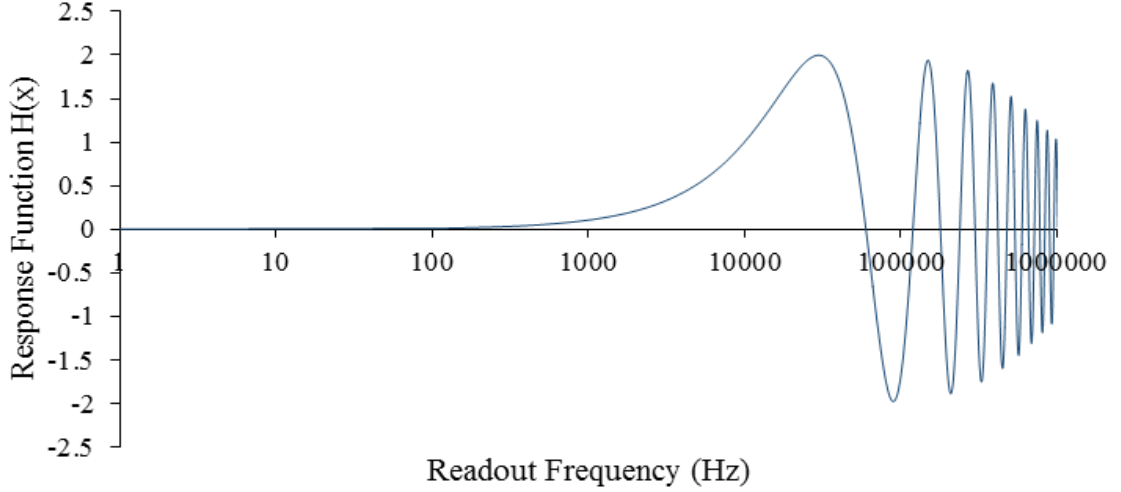


Figure 2.24: An example sample response function. The plot shows how the response function varies with sampling frequency.

Figure 2.25 shows the resultant read noise, δ_{read} , that is not attenuated by the double delta sampling technique (sometimes referred to as a clamp-and-sample technique) as a function of sampling frequency (and therefore a given readout frequency), where δ_{read} is given by Equation 2.9 (Hopkinson and Lumb 1982),

$$\delta_{read}^2 = \int_0^{\infty} N^2(f) H^2(f) df \quad 2.9$$

where $N(f)$ is the noise function (Figure 2.22) and $H(f)$ is the sample response function (see Figure 2.24).

Both $H(f)$ and $N(f)$ depend on the sampling frequency of the system so by integrating over an appropriate range of sampling frequencies the total read noise (in terms of V) can be obtained. The read noise in electrons, $\delta_{read} e^-$ is given by Equation 2.10,

$$\delta_{read} (e^-) = \frac{\delta_{read} (V)}{Resp \cdot A} \quad 2.10$$

where $Resp$ is the responsivity of the CCD on-chip amplifier (see Section 2.2.1) and A is the gain introduced by sampling system.

The gain is given by Equation 2.11

$$A = 1 - e^{\left(\frac{\text{bandwidth}}{f_{\text{sampling}}}\right)} \quad 2.11$$

where f is the sampling frequency. It is clear from Figure 2.25 that the overall read noise is relatively flat as a function of frequency until $\sim 250\text{kHz}$, then increases by a factor of 3 by 1MHz .

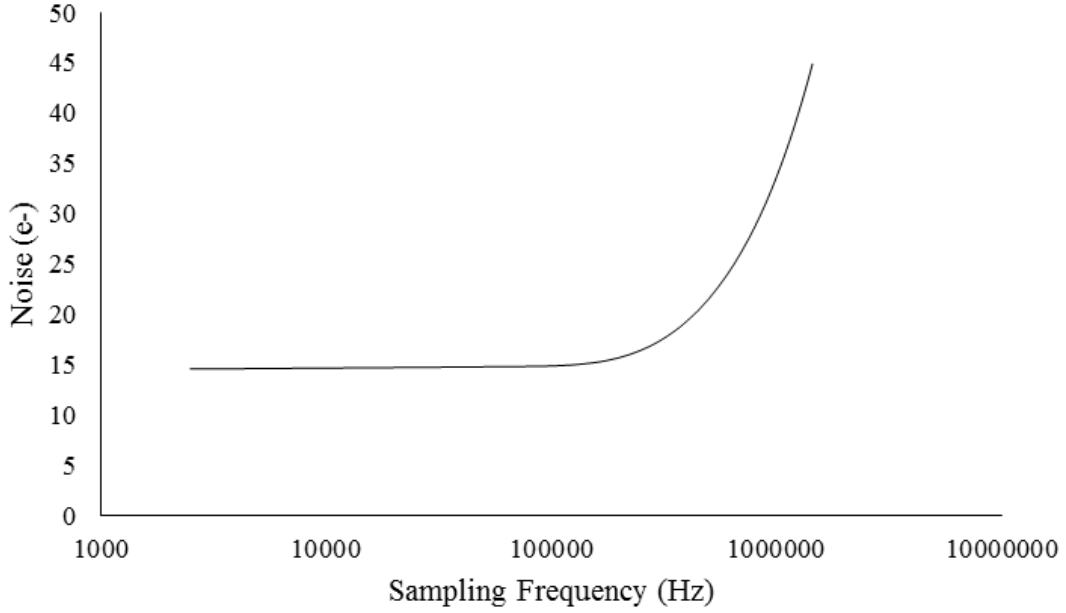


Figure 2.25: A plot to show the read noise as a function of sampling frequency. The plot was produced by integrating the noise function squared multiplied by the sampling function squares, over all possible analogue frequencies. The read noise value for a given sampling frequency is the resulting sum of all noise at all frequencies.

The final aspect of the noise associated with sampling electronics is the ADC quantisation noise, δ_{quant} . When the sampled signal from each pixel is digitised, there is a level of uncertainty in the resulting digital number. This uncertainty is usually referred to as quantisation noise and is the RMS of the ADC transfer function shown Equation 2.24.

The quantisation noise is $1/\sqrt{12}$ in ADC units. In terms of electrons, the noise depends on the gain of the system i.e. the number of electrons per digital number (DN). The conversion between electrons and ADC units is given by Equation 2.12,

$$e^- \text{ per DN} = \frac{S_{\text{max}}}{2^n - 1} \quad 2.12$$

where S_{max} is the maximum CCD signal in electrons and n is the number of digitisation bits produced by the ADC. The quantisation noise is added in quadrature to the read noise (obtained from Equation 2.11) to give a total read noise (Equation 2.13),

$$\delta_{total\ read} = \sqrt{\delta_{read}^2 + \delta_{quant}^2} \quad 2.13$$

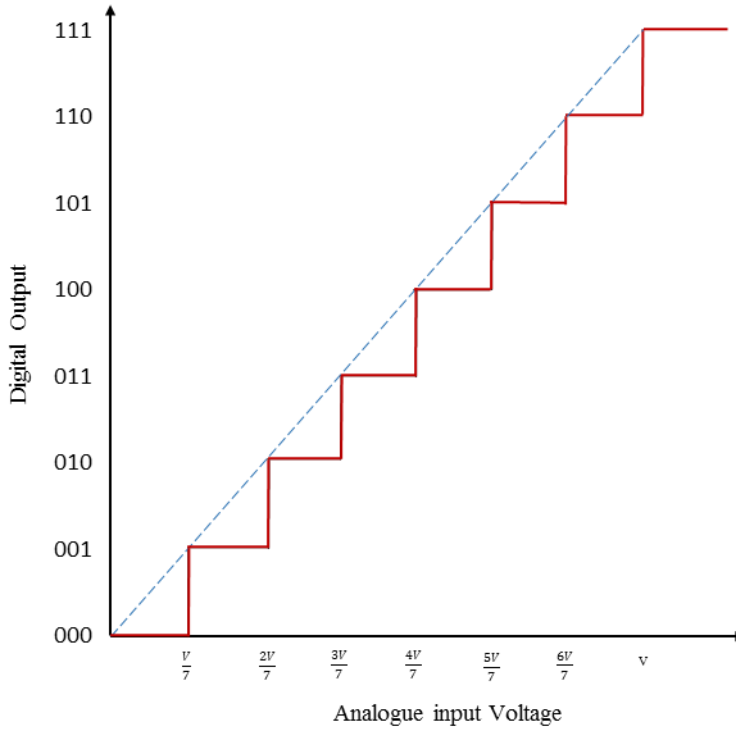


Figure 2.26: An ADC transfer function.

Dark noise

Dark noise is caused by imperfections and impurities in the silicon and on the silicon-silicon dioxide boundary. At these sites there are states between the valance and conduction band that would otherwise be forbidden; these states are known as traps. Thermal energy excites electrons into these states where they can easily be excited into the conduction band where they are accumulated in addition to the signal. These states have characteristic energies and timescales (on which they capture and release electrons from the valence band into the conduction bad), which are highly dependent on device temperature. Therefore operating a device at a lower temperatures decreases the thermal

energy of the electrons and increases the time scales on which they are captured and released from and into the pixel.

The noise associated with the dark current generation process, dark current shot noise (δ_{dark}), is given by Equation 2.14,

$$\delta_{dark} = \sqrt{I_0 t} \quad 2.14$$

where I_0 is the dark current per second and t is the integration time. However, not all pixels will have the same level of dark current. This variation is called dark current non-uniformity. Dark current levels can vary by 3-10% RMS over the device. Dark current levels also depends on integration time (the longer the integration time, the longer there is for dark current electrons to build up within the pixel).

Surface dark current

Since many of the traps are located at the silicon-silicon dioxide boundary, it is possible to reduce their effect by implementing dither clocking. Dithering moves the confined charge rapidly between adjacent pixels. Since the traps have very small capture time constants, on average, most of the traps causing the dark current will be neutralised as the charge is shifted between pixels.

The number of traps is reduced during the manufacturing process but some states will still remain. The number of electrons entering the conduction band from these intermediate states (traps) can be reduced by increasing the number of holes at the site to 'neutralise' the electron source. This is achieved by reducing the lower level of the clocks to below the substrate level so that holes from the channel stops are attracted to the Si-SiO₂ layer. These holes fill the traps and suppress the surface dark current. This is known as (advanced) inverted mode operation (AIMO) as the silicon-silicon dioxide surface goes from a p-type to an n-type. To prevent charge from dissipating into the substrate while the clocks are inverted, charge is confined by an additional implant barrier situated under one of the parallel clock phases. AIMO devices do not exhibit high full well capacities because extra components are required at the pixel level to invert the clocks and additional substrate material in the device. If using a Non Inverted Mode Operation (NIMO) device

then the substrate voltage is increased (this pulls the holes towards the surface like before).

Bulk dark current

Electrons that are generated by thermal excitation in the bulk depletion region of the silicon are known as bulk dark current. Many are as a result of metallic impurities and imperfections that can be reduced in the manufacturing stages (Janesick, 2001). However the bulk dark current can be suppressed and can contribute very little to the overall dark current if a device is cooled (see *Dark Noise* section).

Thermoelectric Cooling

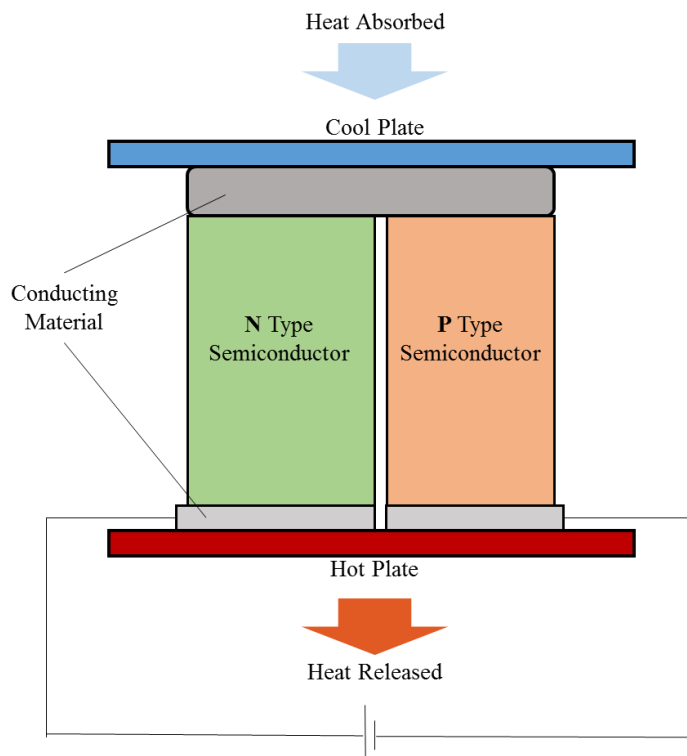


Figure 2.27: A diagram of a thermoelectric cooler.

To reduce the dark current and its effects, CCDs are often cooled. A common method of cooling is through the use of thermoelectric coolers (TECs). TECs are based on a physical phenomenon known as Peltier cooling. A TEC module consists of two material blocks; an n-type and a p-type semiconductor, each made from doped bismuth telluride. The two materials are connected at one end via a conducting (usually copper) bridge, to form an n-p junction. The semiconductors are placed in a series circuit (as seen in Figure 2.27)

with the n-type material connected to the negative potential and the p-type connected to the positive potential side of the voltage supply, usually via a second slab of thermally conductive material (Lundstrom and Jeong, 2013).

When a voltage is supplied to the circuit, the electrons in the n-type material and the holes in the p-type material flow towards the semiconductor junction. In this configuration, all charge carriers flow in the same direction, carrying thermal energy from the bottom of the system towards the top. The bottom slab quickly becomes cooler as heat is ‘pumped’ towards the top slab, where if there is a sufficient heat sink (such as flowing water or a large block of conducting material), it will be conducted out of the system. The rate of change in temperature depends on the number of mobile charge carriers, i.e. the type of semiconductor materials and the operating voltage. In addition, if the polarity of the circuit is reversed, the pumping direction is also reversed and the temperature of the cold junction will begin to increase.

Thermoelectric coolers are created from an array of the modules described above, connected by two metallic layers (to provide the junctions) and sandwiched between ceramic substrate. The ceramic material provides electrical insulation to the heat sink and object (or device) that is being cooled. TECs have an average operating lifetime of 100,000 hours and contain no moving parts, unlike methods such as air cooling.

Radiation Damage

Radiation damage is a very important issue concerning imaging devices that operate in a space environment. There are several types of radiation damage that can affect the operation and efficiency of a CCD. The first is ionising radiation. This radiation is composed of protons, neutrons, electrons, photons (X-rays or gamma rays) and heavy ions that have enough energy to move an electron from the atomic valance band into the conduction band, hence creating a trap. These traps can change bias voltages within the device. Bias shifts of up to 2V can be tolerated by accounting for the voltage changes before launch and during the mission. Traps created in the Si-SiO₂ can also increase the dark current (see *Dark Noise* section of this chapter).

Displacement radiation damage comprises energetic particles like protons, neutrons and heavy ions that collide with the silicon atoms within the device and displace them. This

creates a lattice configuration where both atoms and gaps (vacancies) are in the wrong place. Many of these displacements just shift back or recombine but some vacancies link with phosphorous atoms to create electron traps. These traps degrade the charge transfer efficiency. A trap will capture an electron (quickly) and release it sometime later, creating image smear. These traps will also increase the bulk dark current in localised areas, known as hot pixels.

Displacement damage is also known to induce Random Telegraph Signals, randomly fluctuating charge levels with time periods dependent on temperature. As the temperature is decreased, the time constant increases, making this source of noise less of a problem.

Finally, cosmic rays pass through the device, ionising charge along its path. This is called a transient effect. Usually, no lasting damage is caused but the short term effects can have an effect on returned data (due to short term signal increase). However, data extraction techniques can identify these defects as they are rarely seen in two consecutive frames.

2.2.2 INTENSIFIED CCD

Often when incident light levels are low, intensified CCDs are required since standard devices do not have the sensitivity required to detect the low level signal above noise levels. This is typically true in the case of stand-off Raman spectroscopy applications. Due to the larger operating distance and inherent low intensity of Raman scattering, signal levels can be particularly low compared to in situ Raman applications. In these cases, an intensified CCD allow for the detection and measurement of a very low light levels (single photons in the case of some detectors). The following sections discuss a number of intensified CCDs and the role they play in Raman spectroscopy instrumentation.

Microchannel Plate devices

An intensified CCD converts the incident light into photoelectrons, which are then passed directly or through a phosphor screen to the CCD where they are collected and measured (see a description of measurement process in the previous section). During this process the electrons are intensified by a microchannel plate (MCP). An MCP is a collection of

short glass fibres (a few millimetres in length), bundled together in parallel to create a thin cylindrical plate, as illustrated in Figure 2.28. Each fibre is 4-25 μm in diameter and coated on the inside with a semi-conducting material. In the case of intensified CCD detectors, image photons are initially incident on a photocathode (which has a voltage of 800V with respect to the associated anode). When struck by photons, the photocathode emits a photoelectron. The front (input side) of the MCP is held at a voltage of 1kV compared to the output side, so the photoelectron is accelerated through one of the microchannels. The microchannels are angled compared to the direction of the electron, creating a high probability of a collision with the channel wall. When bombarded with electrons, the semi-conducting material on the inside of the tube emits a cascade of electrons, proportional to the initial energy of the electron (and hence the incident photon) and the potential difference across the plate. On exiting the MCP, the electrons collide with a phosphorous screen. As the electrons decelerate and lose energy they emit photons with a wavelength proportional to their collision energy. This light is then focussed onto a CCD to be integrated and measured.

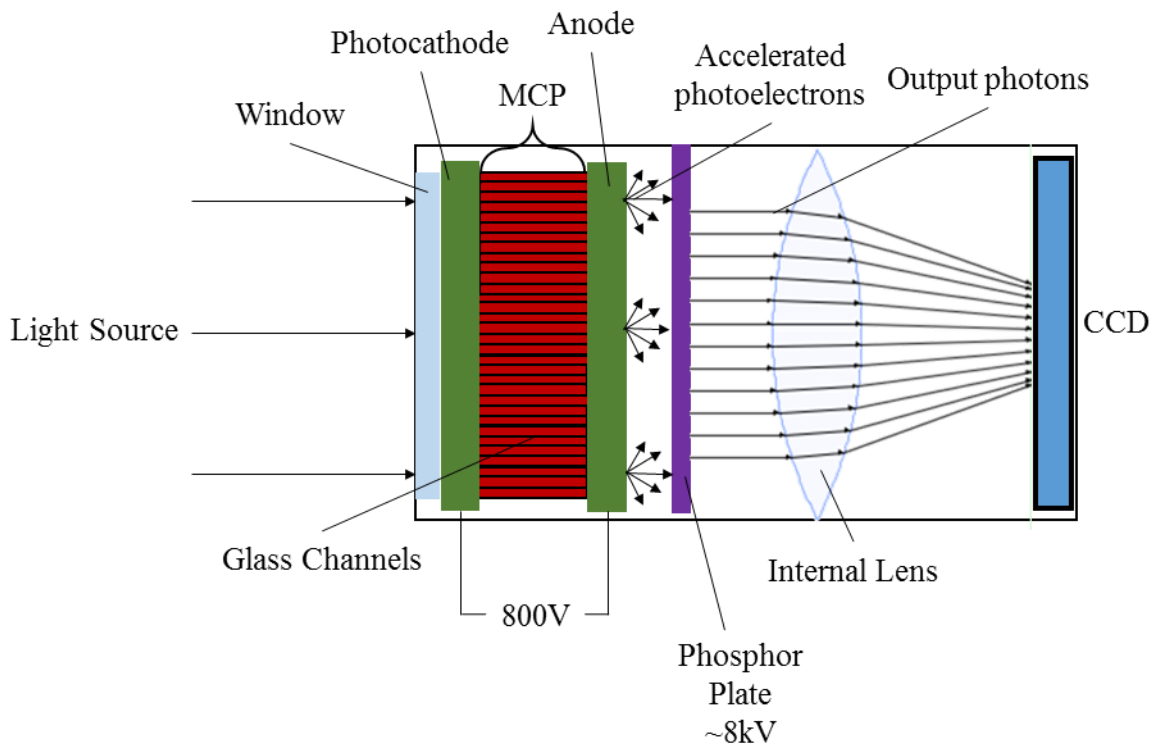


Figure 2.28: A schematic of a microchannel plate, coupled to a CCD.

The amplification factor achieved by these devices can be of the order 10^4 , making it an excellent method of intensifying low signal levels. Overall the electron path through the system is very short, making the response time for MCPs very short and ideal for pulsed laser gating systems. An example of an intensified device is the P-MAX4 developed by Princeton instruments. In addition, the photocathode can act as an electronic shutter. By dropping the cathode voltage to 0V temporarily, incident photons will not be intensified, 'shuttering' and gating the detector system. As discussed in Chapter 1, Section 1.3.2, this is one method of reducing the fluorescence and ambient light (signals that obscure the detection of Raman photons) detected by the stand-off system. However, MCPs are expensive, fragile and can be damaged by over exposure to light. The high operating voltages (800V and 1kV for the photocathode and MCP) also make intensified detectors difficult to space qualify. Intensified detectors do not currently have a high Technology Readiness Level (TRL) compared to other detectors.

Electron Multiplication CCDs

Electron Multiplication CCDs have been developed to detect low signals without the need for a separate photon multiplier (such as an MCP). EMCCDs are based on frame-transfer CCDs, which are discussed in Section 2.2.1. After charge has accumulated in the image area pixels, the charge is rapidly shifted into the storage region. Once in the storage region, each row of charge is shifted into the serial register to be read out, pixel by pixel. In an EMCCD however, there is an additional multiplication register (following the serial register), as illustrated in Figure 2.29. As the charge is clocked through the multiplication register, there is a small probability that additional electrons will be created through impact ionisation. If an electron has sufficient energy it will create an electron-hole pair in the substrate. The charge is clocked through the multiplication register to the output amplifier. In this configuration, the signal has been multiplied before read noise has been added to the signal (e2v technologies 2003).

Initially, there is a very small chance that electron multiplication will occur in the multiplication register. However, to increase the chances of an electron collision with the substrate, the charge is clocked through the register at a higher (variable) voltage, compared to a standard serial register, which increases the energy of the initial electrons. The charge is also clocked through many hundreds of pixels before reaching the output

amplifier, further increasing the chance of charge multiplication. Cooling the detector also increases the probability of electron multiplication. For example, a device at 50°C with a clock voltage of 45V achieves a gain of 1000 (e2v technologies, 2011) compared to a standard non-intensified CCD.

One advantage of an EMCCD is that it can be used to detect both low and high levels of ambient light (unlike an MCP which is prone to damage). However, an EMCCD cannot be gated in the same fashion as an MCP. Although, as discussed in Chapter 1, gating is not always necessary for a Raman application if the signal is high enough to overcome the fluorescence and ambient light levels. An example of an electron multiplying detector is the L3 CCD97-00 device developed by e2v (e2v technologies, 2011).

Electron multiplying devices can also be operated in inverted mode to reduce surface dark current, however this device architecture is affected by Clock Induced Charge (CIC). As charge is clocked through image pixels towards the readout register, there is a small probability that the shifted charge can knock additional charge into the pixel via impact ionisation. CIC does occur in non EMCCDs too but the effects are usually minimised to

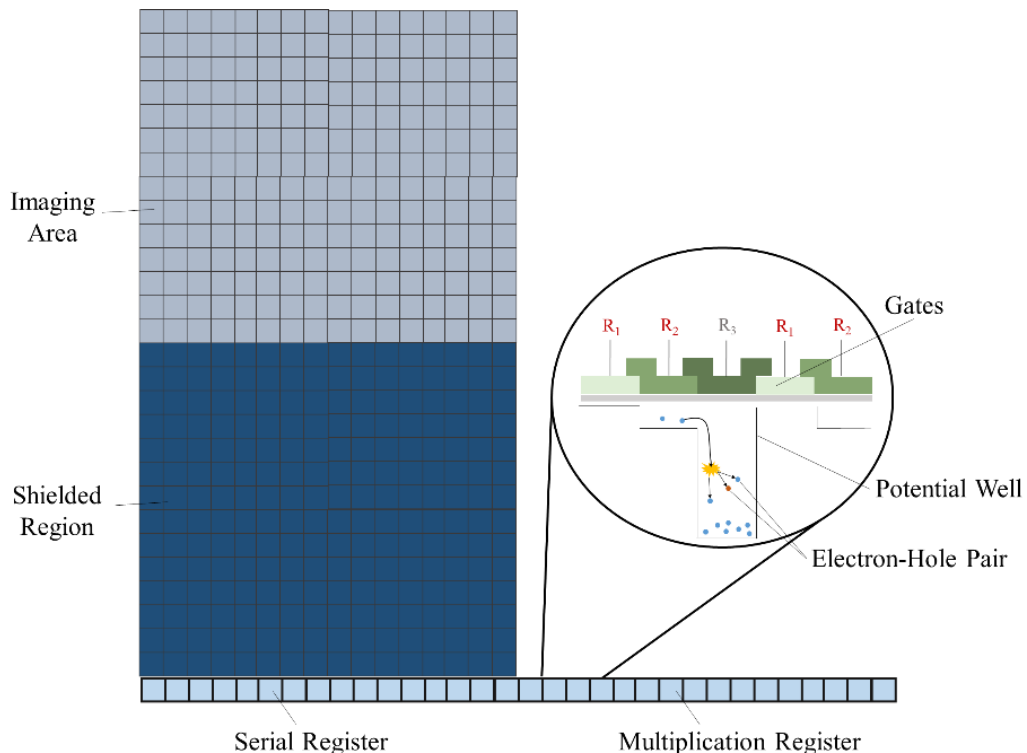


Figure 2.29: A diagram of an EMCCD. Compared to a standard frame transfer CCD, the EMCCD contains an additional multiplication register, through which charge is clocked before it is transferred onto the sense node. The insert shows the larger potential differences that are employed to increase the chances of ionisation in the CCD substrate.

1 in 200 pixels (Denvir and Conroy, 2003). The effect becomes more predominant when binning a large number of pixels but the noise associated with CIC is insignificant compared to read and dark current noise. In EMCCDs however, the CIC is multiplied along with the signal and can therefore become a significant issue.

2.2.3 CMOS

Similar to a CCD, a CMOS (complementary metal-oxide semiconductor) device is fabricated using monolithic silicon, divided into a number of physically separate imaging regions (pixels). Charge generated by the photoelectric interaction of a photon with the detector material is held in a pixel by a potential created by a high voltage. However, each pixel in a CMOS device (often) has its own integrated charge-to-voltage circuitry. This circuitry often includes amplifiers, noise-correction components and digitization circuits and therefore a CMOS chip outputs digital data (Yadid-Pecht and Etienne-Cummings, 2004). Consequently, unlike a CCD, there is no need for further digitisation circuitry. A diagram of a CMOS detector illustrating the layout and structure of the device is given in Figure 2.30.

This unique structure gives the CMOS detector many advantages over the CCD device. Since there is no need to shift charge into other pixels when reading signal levels, CMOS devices are inherently more radiation tolerant than CCDs. They are easier to manufacture and for a reasonably low cost given their size. The individual digital image sensors also allow for single pixel access, therefore windowing (reading out only select regions of the device) is easy to implement. In addition, the smaller dynamic range of a CMOS device means they inherently run faster (as charge does not have to be integrated for long periods of time), with little impact on read noise. Therefore at larger readout speeds CMOS devices will achieve a better signal to noise ratio. However, at faster read out speeds the read noise from a CCD will be larger (see Section 2.2.1) meaning the equivalent operation of a CMOS device results in a better signal-to-noise ratio. Consequently, a CMOS detector would potentially have a low read noise advantage for Raman applications if it were required to obtain spectra at high speed (perhaps in conjunction with a pulsed laser). CMOS devices also consume a small amount of power but dark current can be an issue because of the additional heat from circuitry.

Until recently, CMOS devices suffered from low quantum efficiency compared to CCDs due to the metal and dielectric layers on the top of the substrate which absorbed much of the incident light. This would have been a potential issue for Raman instruments which are required to detect low signal levels, such as a stand-off instrument operating over a large distance. However thinned and back-illuminated CMOS detectors are now quite common (although not readily accessible for commercial uses) which exhibit a QE comparable with back-illuminated CCDs.

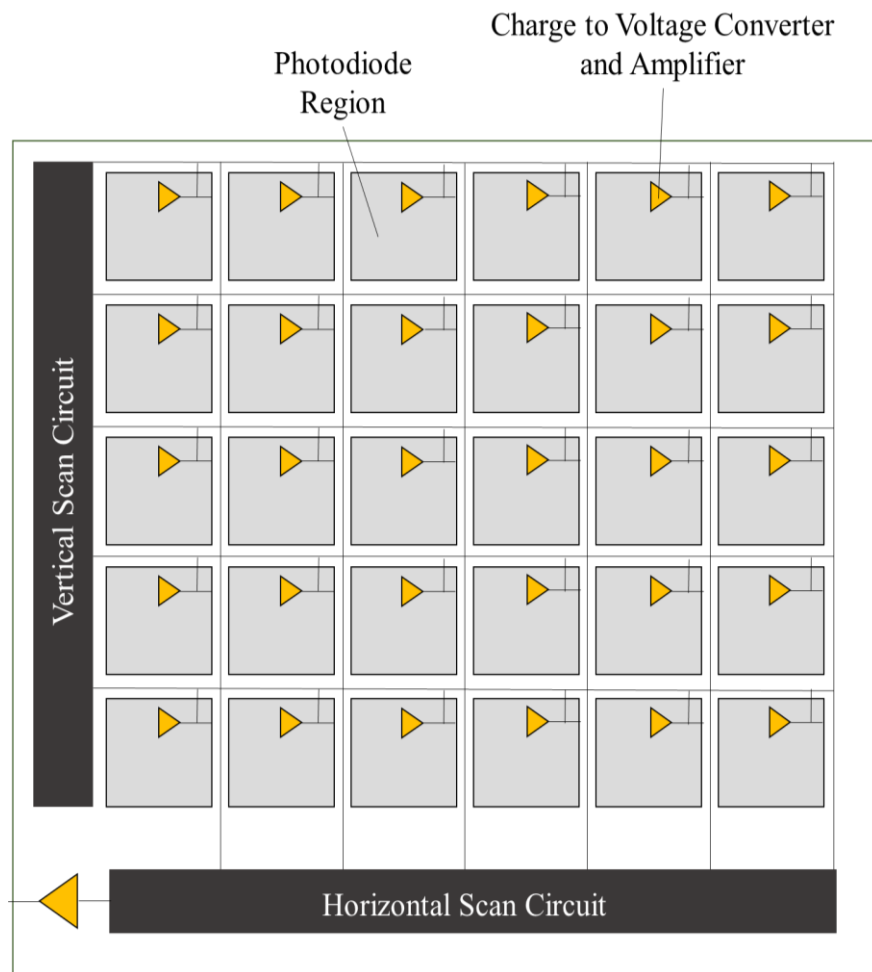


Figure 2.30: A diagram showing the layout of a simplified CMOS device. Each pixel contains a photon detection element, a charge to voltage conversion circuit, an amplifier and a switch. The switch allows the user to read only selected pixels, instead of an entire row (similar to a CCD)

2.2.4 SCINTILLATORS

Scintillator detectors are frequently used to detect high energy photons. They are fabricated from materials, which, when struck by high energy ionising photons (such as X-rays), emit lower energy photons, which in turn are collected and converted to an electrical pulse via a photomultiplier tube (Saha, 2001).

The scintillation element consists of a crystal, such as sodium iodine (NaI), doped with Thallium (Tl); the crystal material can be changed to also detect alpha and beta particles (Saha, 2001). A fraction of the ionizing photons that are incident on the crystal are absorbed and excite electrons within the crystal structure to a higher energy state. After a short time, the electrons decay to a lower state, emitting a photon. However, the addition of Tl in the NaI structure means the energy difference between the upper and lower states is probably smaller than that of a pure NaI crystal, therefore the photon emitted as a result of the interaction will be of a longer (visible) wavelength compared to that emitted by NaI (Choppin, Liljenzin and Rydberg, 2014).

Following the scintillator crystal is a photomultiplier tube, as illustrated in Figure 2.31, which incorporates a photocathode, electron multiplier and an anode. The visible photons produced by the scintillator are collected by the photocathode. The photocathode then emits a number of low energy electrons proportional to the energy of the incident photon. These electrons are accelerated towards the anode. On collision with the anode, the high energy electrons generate secondary electrons. The potential difference between the

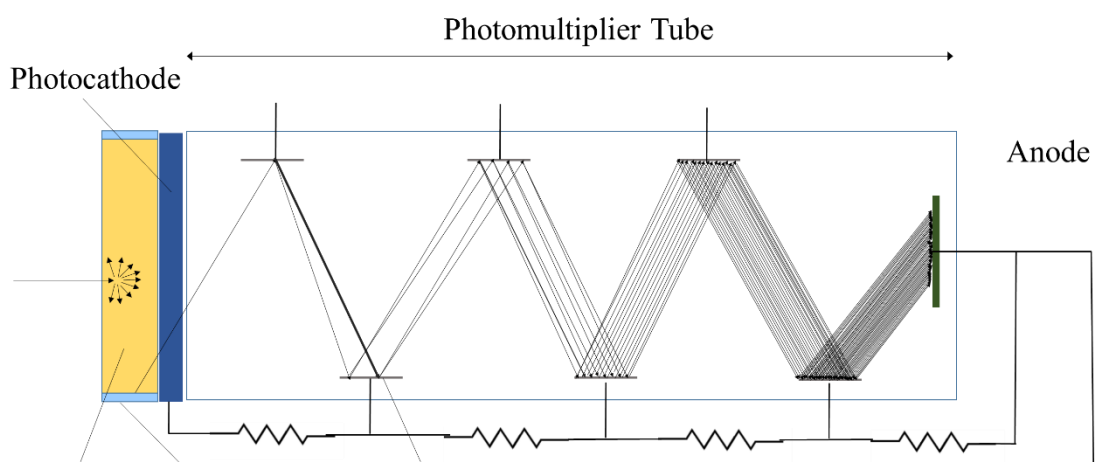


Figure 2.31: A schematic of a scintillator. The diagram shows the increasingly high voltage that is applied through the PM tube in order to accelerate and multiply the electrons.

electrodes is proportional to the electron multiplication factor (gain) (Phelps, 2006). The electrons collected by the anode give rise to a large pulse in current. The magnitude of the pulses are then measured and counted to determine the distribution of incident photon energies.

An efficient scintillator converts most of the incident particles into photons to be detected by the photocathode. The scintillator should also be transparent to its own light and have a minimum refractive index to enable the photocathode to collect as much signal as possible. The thickness of the photocathode will also affect the efficiency of a detector. Electrons generated in a thicker substrate will lose energy (and therefore become trapped) before exiting into the vacuum due to interaction in the cathode and anode material.

Although scintillators are often used as high energy (X-ray and gamma) radiation detectors, there are certain circumstances in which they could be considered for Raman instrumentation. For example, the photomultiplier tube offers a signal amplification, which would be beneficial to a stand-off Raman system, where the incoming signal is relatively low. However, similarly to the intensified CCD, the high operational voltages can be problematic when qualifying the detector for space missions.

2.2.5 PHOTODIODE ARRAY

Another type of multichannel detector is the photodiode array (PDA). Similar to a CCD, PDAs are fabricated from a silicon semiconductor substrate. A photodiode consists of a p-n junction that operates under a reverse bias. The reverse bias (between the cathode and anode) forces free electrons and holes to migrate towards the p-type and n-type material respectively, creating a depletion zone. This is illustrated in Figure 2.23. In the case of a PIN junction, the depletion zone is formed in the intrinsic layer between the p and n-type materials. Incident photons with sufficient energy generate electron-hole pairs within the depletion zone, which are then immediately separated due to the reverse bias. This movement of charge results in a photocurrent that is linearly proportional to the incident photon energy. In a PDA, thousands of these individual photodiodes are arranged linearly, connected by a common cathode. Each photodiode has its own anode which can be selectively addressed in order to measure the induced photocurrent.

In comparison with CCDs, PDAs require a much larger voltage across the semiconductor. CCD pixels are also typically smaller than the photodiodes found in a PDA, ultimately enabling a higher spectral resolution. CCDs also have a higher charge-to-voltage conversion efficiency; due to the higher output capacitance of a PDA, the read noise is typically 100 times that of a CCD (Chim, 2000). Therefore, to achieve a high SNR, the incident light level must be considerably higher than that required for a CCD. In a low light level application, PDA devices are used in conjunction with intensifiers such as MCPs. PDAs have a very wide spectral response (200-1100nm) (Ewing, 1997) and due to the lack of operation circuitry on the surface (compared to CCDs and CMOS devices) they have a relatively high quantum efficiency (Webster and Eren, 2014).

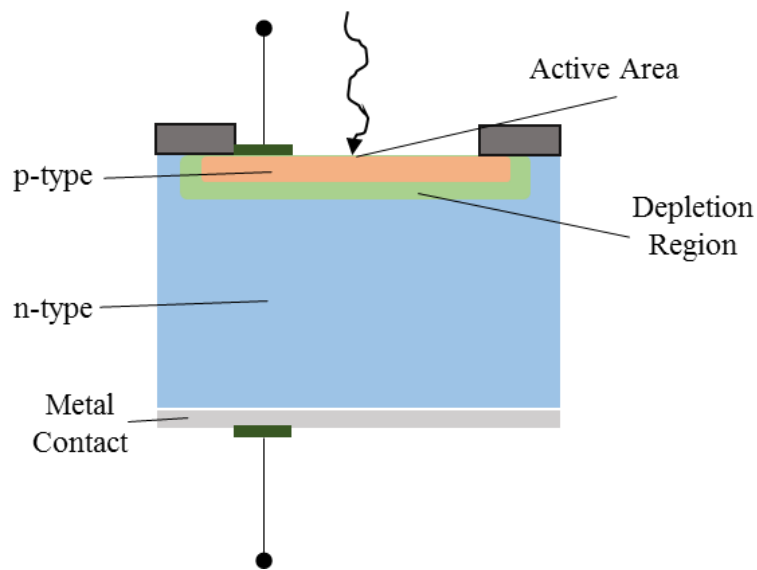


Figure 2.32: A schematic of a photodiode. Many of these devices are combined within to form a photodiode array detector.

Photodiode arrays can also be operated at high speed and have been used for femtosecond Raman analysis (Fang *et al.*, 2009). If the signal collected by a planetary Raman instrument was sufficiently high (so as to not be affected by the high noise levels exhibited by a PDA) then PDA detectors could be utilised and fast acquisition of Raman would enable temporal separation of the signal produced by the highly fluorescing samples (see physical process discussion in Chapter 1, Section 1.3).

2.2.6 AVALANCHE PHOTODIODES

Avalanche photodiodes (APDs) are based on PIN or P-N photodiode detectors. With a similar architecture to photodiode detectors (as illustrated by Figure 2.33), APDs are also operated with a large reverse bias (up to 2.5kV). The large bias voltage means the electric field between the cathode and anode is substantially stronger than that of a photodiode detector. Electron-hole pairs produced in the depletion zone, via absorption of incident photons, are accelerated through the p-type material (holes are also accelerated towards the n-type material). Under a large potential difference, the charge carriers are more likely to collide with the crystal lattice and induce further electron-hole pair generation. These secondary charge carriers are subsequently accelerated towards the electrode and, depending on the bias level, will induce further charge multiplication. The final multiplication in charge is referred to as Gain and is proportional to the bias between the electrodes. However, due to the design of the p-n junction, there is an upper limit to the bias voltage and therefore the gain of the detector. If the bias exceeds the breakdown voltage of the intrinsic layer then the gain is no longer linearly proportional to the applied

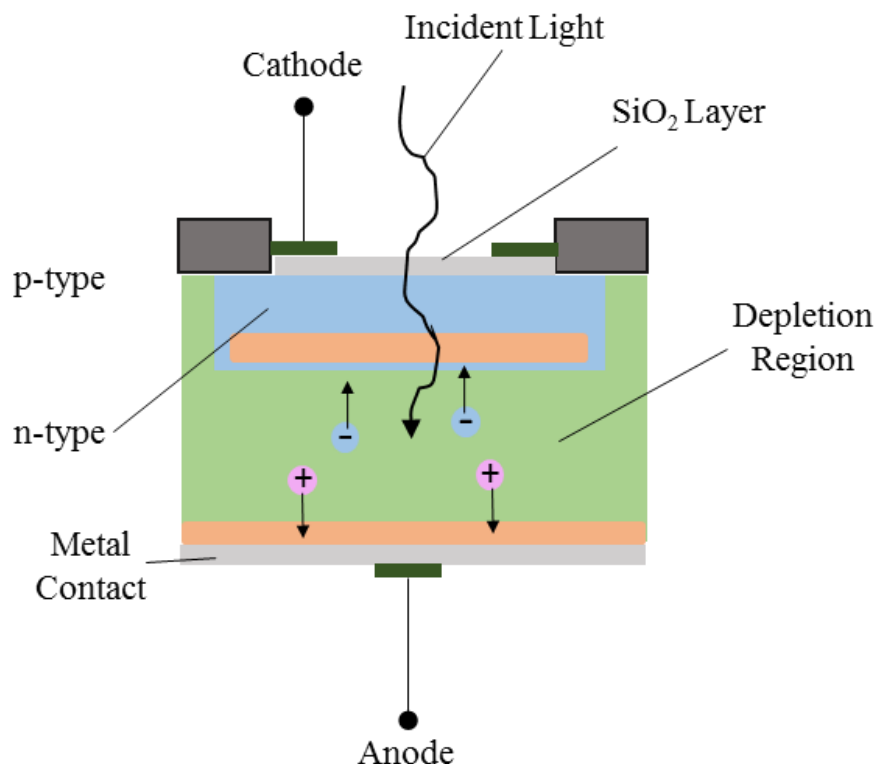


Figure 2.33: A diagram of an avalanche diode detector.

bias. Usually APDs are operated just under this upper limit so they are often very sensitive to external operating conditions.

Similar to scintillators and intensified photodiodes, the inherent signal amplification process that occurs within these devices is beneficial to systems that are required to measure relatively low signal, such as those from a Raman instrument. Avalanche detectors can also be operated at high speed; Blacksberg et al (2011) demonstrated they were able to use avalanche detectors to acquire Raman spectra while temporally avoiding fluorescence emission from a sample.

2.2.7 DETECTOR SUMMARY

This section has described the various methods to accurately detect and measure a Raman signal acquired by an instrument. Table 2.5 summaries the key features of five CCD detectors and includes a CMOS detector for comparison.

Name	Type	Array Size (H) x (V)	Full Well Capacity/Hz (typical)	Read out speed/ Hz (typical)	Read noise/ e-	Temperature (K) *	Quantum Efficiency, %	Spectral sensitivity/nm	Intensified?
Sony ICX285AL	CCD	1360 × 1024	25,000	28.64 M	4	unknown	65 (uncoated)	360 – 1100	No
CCD230-10	BI Multiple output nodes	2048 x2064	150,00	500k	9	230	55-50	300-1060	No
CCD230-42	BI Multiple output nodes	2048 x 2064	150,000	1000K	8	230	85 (mid band coating)	300-1060	No
CCD47-20	BI Frame transfer operation.	1024 x 1033	100,000	500k	6	229	85 (mid band coating)	200-1100No	No
CCD42-40	BI Full frame device	2048 x 2052	100,000	500k	6	229	85 (mid band coating)	200 – 1060	No
CCD30-11	P-Max4	1024 x 256	700,000	45k	5	229	75 (broadband coated)	200–1100	Yes- MCP
CCD201-20	BI Frame transfer	1024 x 1024	80,000	500k	3.1	230	>90 (midband coating)	350-1000	L3
Onyx 1.3M – EV76C664	CMOS	1280 x 1024	18,000	622M	18 (maximum)	-	65	-	No

Table 2.5: A table displaying the key parameters of different detectors, in particular, the detectors that will be utilised in this project.

*required to achieve a dark signal of 0.02 e-/pixel/s. BI: Back Illuminated

INSTRUMENT PERFORMANCE

3 SIMULATOR

Chapter 1 described how recent advances in the miniaturisation and robustness of laser and optical technologies have enabled stand-off Raman spectroscopy to play a key role in the planning for future planetary exploration missions (e.g. see Sharma et al. 2003). However, there remain a number of challenges associated with deploying such instruments on rover platforms (see, for example, Angel et al. 2012 for a summary of such challenges). These include the need for complex modes of operation, which are often required to minimize the impact of the various sources of background noise, including: ambient light, sample fluorescence and detector dark signal. Additional complications also arise due to the potential impact of radiation damage on the performance of the detector (and optics), saturation effects in the detector and the limited processor (and memory) resources available to enable intelligent/autonomous instrument operation. In order to understand and optimise the performance of a Raman instrument for a particular application, it is useful to develop a full, end-to-end, radiometric model. A typical radiometric model utilises a number of algorithms to describe the transmission of light through the instrument subsystems, accounting for factors such as: component losses and efficiencies, (sub) system geometry and temporal variations. The radiometric model provides a straightforward method for investigating the many interrelated subsystem parameters and enables complex trade-offs to be performed. The model is based on mathematical descriptions of the performance of each component (e.g. the throughput of a lens) within each subsystem (e.g. the collection optics). Ultimately, the model provides a theoretical signal-to-noise ratio based on all of the performance factors associated with each subsystem. These SNR values provide a method of comparing an instrument's

overall performance (as well as each subsystem) for a range of different applications, configurations and operating modes.

The first part of this chapter describes each of the component subsystems in the stand-off Raman system developed for this study. A description of the radiometric model and the individual algorithms that allow a quantitative prediction of an instrument's performance is then given along with details of a general software environment (in which the radiometric model has been developed). The software environment was created to enable end-to-end control of a laboratory or field based Raman spectrometer in order to collect data and verify the radiometric model.

3.1 THE INSTRUMENT

3.1.1 SYSTEM CONFIGURATIONS.

Six different instrument configurations are considered in this study, which can be split into two separate groups with regard to the system working distance (i.e. stand-off or in situ systems). Accounting for a full range of operating distances not only allows for configuration comparisons but enhances the overall capability and practicality of the model with regards to the general overall performance of a Raman instrument.

These two fundamental configurations can then each be described in terms of the type of excitation source used (i.e. continuous or pulsed laser) and the type of detector used (e.g. gated or non-gated). Table 3.1 shows a summary of the six different configurations. The table also reports the collection geometry of each particular configuration, which, as explained in Chapter 2, can have a large impact on the throughput of a system. The oblique configuration (see Chapter 2, Section 2.1.2) was used in the majority of the studies presented here, as it maximises the intensity of the excitation source at the sample and is based on a simple optical set up. For comparison, configuration number 4 considers a co-axial geometry where the continuous laser was redirected through the optical probe head (see Figure 3.2). That is, the excitation light was projected onto the sample via the same optics that were used to collect the Raman scattered light. Diagrams of all six configurations are provided in Figure 3.1 and Figure 3.2.

Configuration no.	Working distance	Collection geometry	Laser type	Detector type
1	Stand-off	Oblique	Continuous	Non-Gated
2	Stand-off	Oblique	Pulsed	Non- Gated
3	Stand-off	Oblique	Pulsed	Gated
4	In situ	Co-axial	Continuous	Non-Gated
5	In situ	Oblique	Pulsed	Non-Gated
6	In situ	Oblique	Pulsed	Gated

Table 3.1: A summary of the different instrument configurations used during this study in order to account for the effects of many interchangeable parameters.

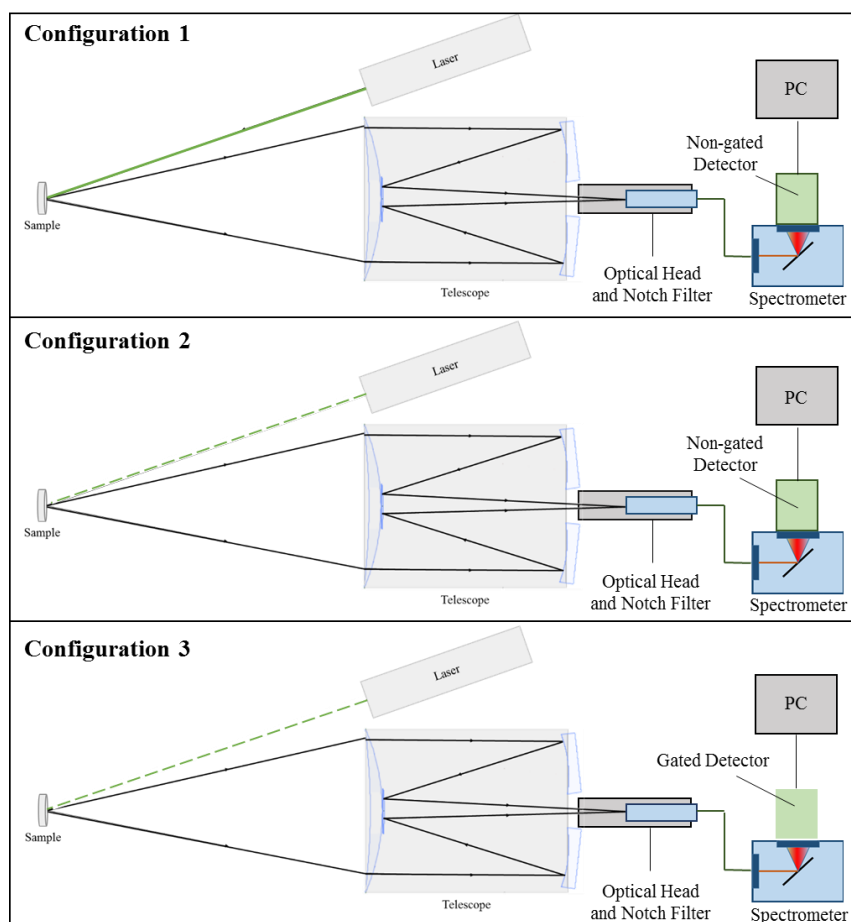


Figure 3.1: Schematics of instrument configurations 1-3.

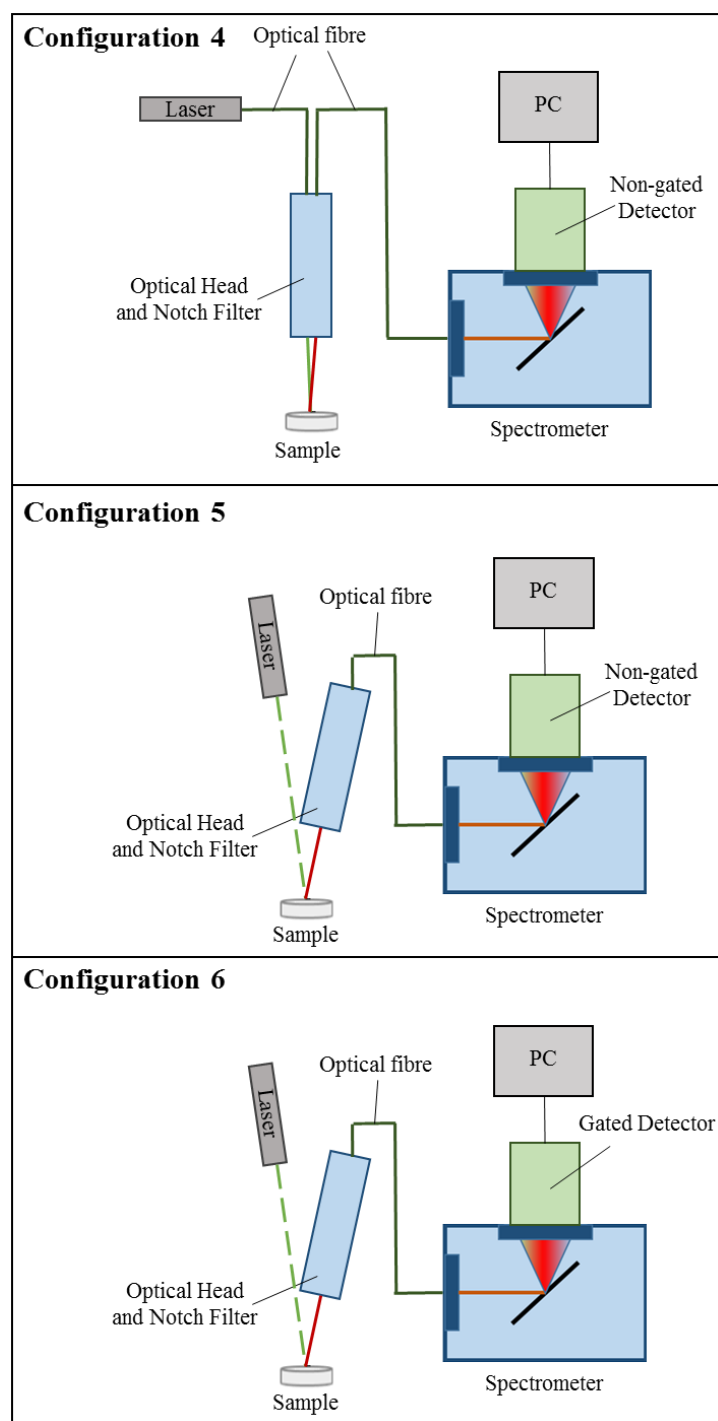


Figure 3.2: Schematics of instrument configurations 4-6

3.1.2 EXCITATION SOURCES

Two excitation sources were used for these studies. The pulsed laser was a Surelite I-10 Nd:YAG laser manufactured by Continuum (see Figure 3.3). The laser operates at a wavelength of 532nm, with a repetition rate of 10Hz in this case. The pulse width was set to ~5ns, with each pulse providing an energy of 35mJ. In this study the pulse energy was limited to reduce the possibility of damage to both the optical components and the sample. The other key properties of the laser (including dimensions) are given in Table 3.2. The laser system was cooled via a closed loop system with water flowing through an air-heat exchanger in order to maintain an operating temperature in the range 18°C -30°C.

The continuous laser was an Excelsior, single mode diode pumped, solid state laser manufactured by Spectra-Physics (see Figure 3.4). The 100mW laser produces a 532nm spot and operates with a temperature in the range 10°C-40°C, stabilised using a thermoelectric based cooling system.

Laser	Spectral	Frequency	Beam	Divergence	Optical	Power
	Line Width nm	Drift MHz/°C	Diameter mm		Head W x H x D cm	Supply L x W x H Cm
Surelite I-10	< 0.03	See Caption	6.0	0.5	77.5 x 19.0 x 17.8	62.2 x 28.2 x 50.8
Excelsior	<0.0001	<50	0.32 ±0.02	<2.5	9.5 x 2.8 x 2.8	13.8 x 9.9 x 3.3

Table 3.2: Beam stability and physical dimensions of both the pulsed and continuous laser. The power of the Surelite I-10 is stable to within 5% measured over 8 hours at 17± 3 °C.



Figure 3.3: Photograph of the Surelite I-10 Nd: YAG laser by Continuum along with the accompanying beam separator used in this project.



Figure 3.4: A photograph of the Excelsior DPSS laser used in this study, which provided a continuous wave excitation source at 532nm.

3.1.2 OUTPUT OPTICS

The laser beam produced by the Surelite I-10 optical head is wavelength filtered using a beam separator. The separator consists of two dichroic mirrors, two 1064nm mirrors and two beam blocks, which when configured appropriately block or divert 1064nm photons that would otherwise contaminate the 532nm beam. A diagram of the separator is provided in Figure 3.5.

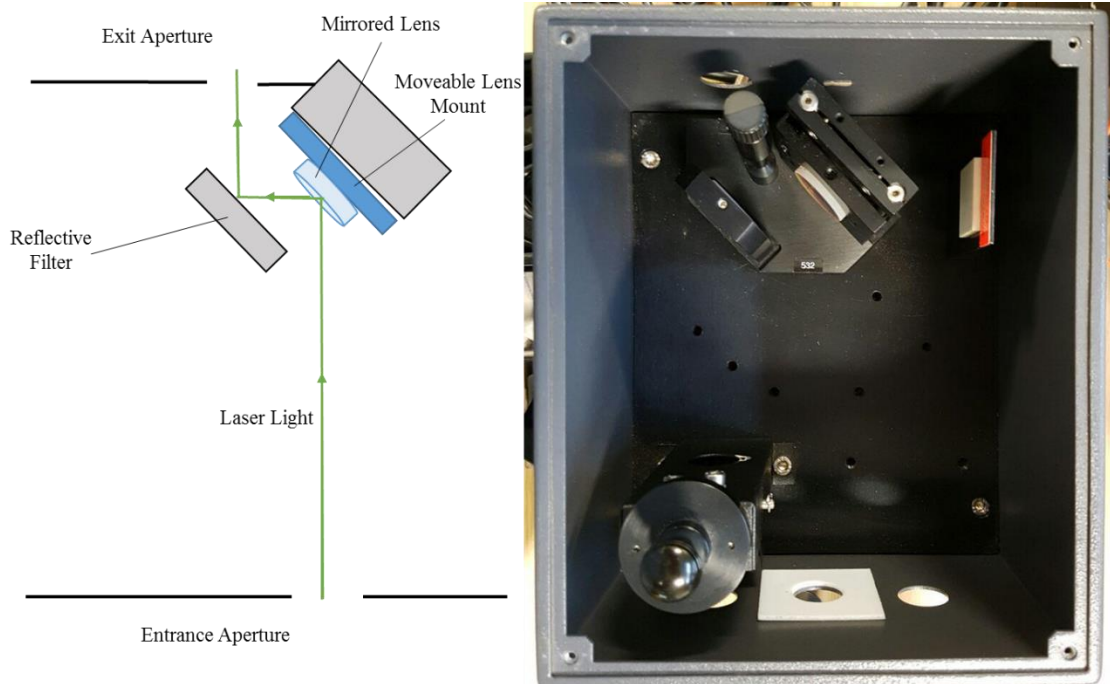


Figure 3.5: Left: A schematic of the beam separator that blocks or diverts additional wavelength light away from the main 532nm beam. Right: A photograph of the beam splitter used in this study.

On exit from the separator, the beam is collimated and focused by two lenses; the first (L1) is a plano concave lens with a focal length of 10 cm which is located at a distance of 1cm from the laser entrance. The second lens (L2) is a bi convex lens with a focal length of 30cm, positioned 10cm from L1 (see Figure 3.6). The lenses are 2.5cm in diameter, have a damage threshold of 7.5Jcm^{-2} at 532 nm (with a spot size of 0.456 mm) and a theoretical transmission efficiency of $\sim 93\%$.

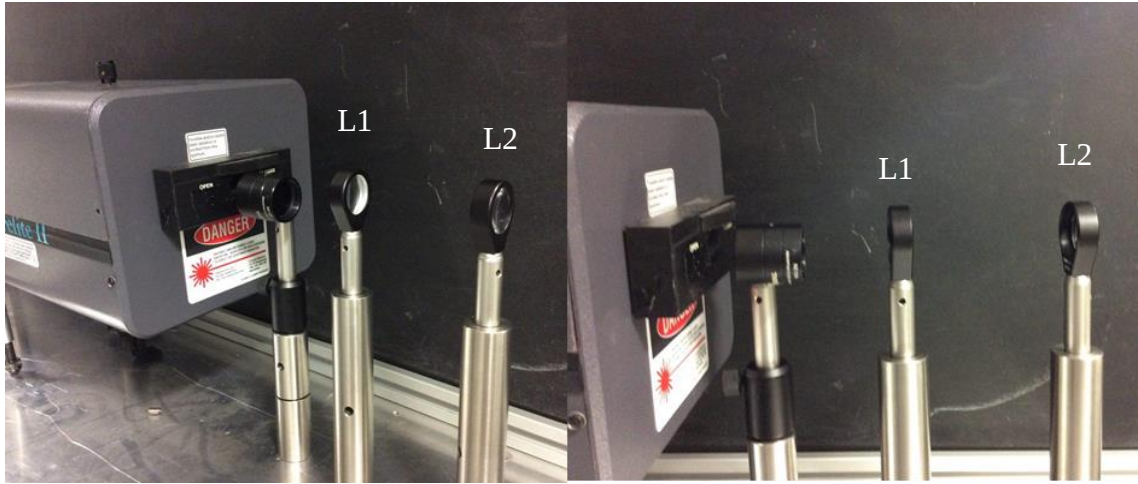


Figure 3.6: A photograph of the optical system used to collimate and focus the laser light to a changeable distance

To aid with focusing and alignment, neutral density filters were used to decrease the beam intensity. These filters were positioned immediately after the beam separator, before the lenses. The filters are 2.5cm in diameter and have a spectral range of 350 - 1100 nm with an optical depth of 0.2 – 4. The filters have a damage threshold ranging from 10 J cm^{-2} for a neutral density of 0.2 to 5 J cm^{-2} for a neutral density of 4.

The continuous laser was focused onto one end of an optical fibre using an M-10X microscope objective (see Figure 3.7). The lens had a focal length of 7.5mm and was coated with MgF_2 to provide a transmission efficiency of $> 90\%$ at 532nm.

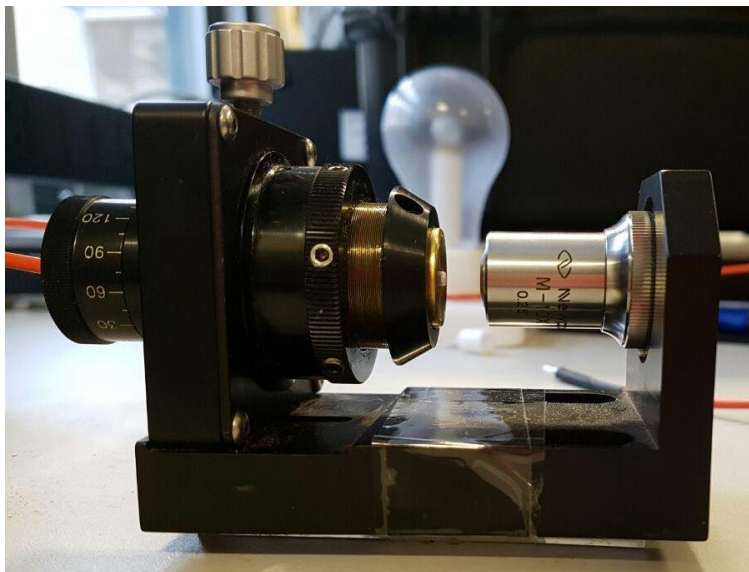


Figure 3.7: A photograph of the M-10X microscope objective used to focus the laser light from the Excelsior onto the end of an optical fibre.

3.1.3 INPUT OPTICS AND COUPLING

The collection optics incorporates a Mead ETX-125 Maksutov-Cassegrain telescope with a focal length of 1900mm (see Figure 3.8). The primary mirror is 138mm in diameter and is fabricated from Pyrex glass. The correcting lens is constructed from BK7 optical glass (Grade-A). The secondary mirror (also made of Pyrex glass) is 39.4mm in diameter and is located in the centre of the correction lens. The overall obstruction of the secondary mirror amounts to ~9.6%.

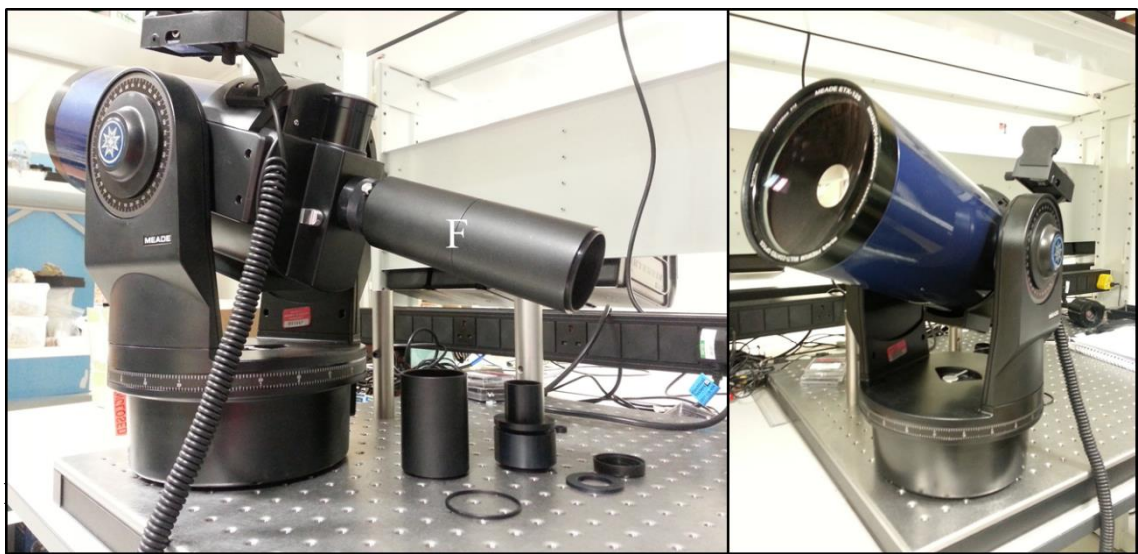


Figure 3.8: To the left, a photograph of the back of the Mead ETX-125 Maksutov-Cassegrain telescope, featuring the extended input optics. On the right, a photograph of the front of the telescope, showing the correcting lens as well as the back of the secondary mirror.

At the focal point of the telescope (point F in Figure 3.8) is a 50.8mm, N-BK7, bi convex lens (L3), AR coated optimum performance in the 650-1050nm wavelength range. The position of the lens is adjusted (and then held) by a 50.8mm lens tube, which attaches to the exit aperture of the telescope via a T-mount adaptor.

The lens tube also incorporates a MultiRxn Probe manufactured by Kaiser Optical Systems Inc. Light is focused from the telescope onto the optical probe via the L3 lens. The 8.0mm aperture to the optical probe is located at the focal length of L3, at a distance of 75.0mm. Light focused into the probe is collimated (L4), filtered and focused onto the end of an optical fibre. The notch filter reflects light at 532nm with an efficiency of 99%, therefore obstructing a large amount of elastically scattered laser light from the sample.

The transmitted light (Raman scattered light and fluorescence) is then focused (using L5) onto a multimode optical fibre (1m in length) situated at the back of the probe. The pointing direction of the telescope (and the subsequent collection optics) was altered using stepper motors that enable horizontal and vertical shifting of the field of view. The full layout of the collection optic system is presented in Figure 3.9.

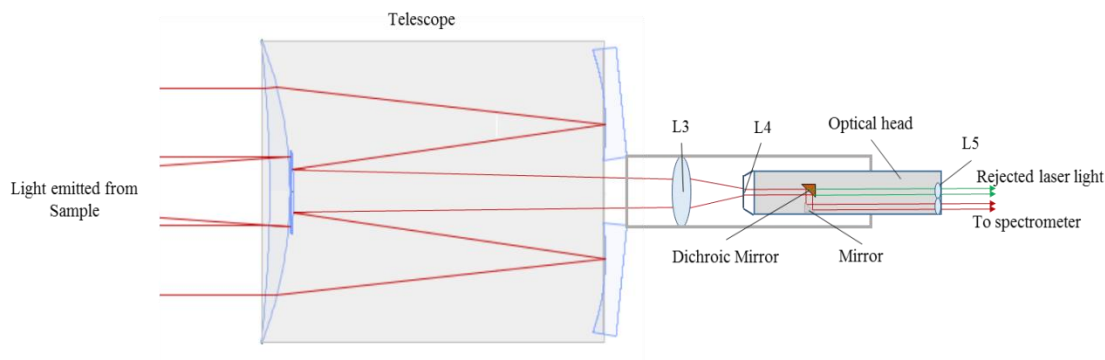


Figure 3.9: A schematic of the input optics.

For operation in the in situ configuration, the laser beam is focused onto the end of an optical fibre using an M-10X objective (see detailed description in Section 3.1.2). The laser beam is internally reflected through the fibre to the probe. The laser light then passes through an aperture at the back of the probe (separate to the aperture that contains the fibre collecting the transmitted, scattered light). The excitation light is blocked by the notch filter (to obstruct any photons that do not have a 532nm wavelength) and is focused onto a sample via the lens at the front of the probe (L4). This set-up leads to a co-axial geometry since the laser light is emitted from almost the same angle and aperture as the

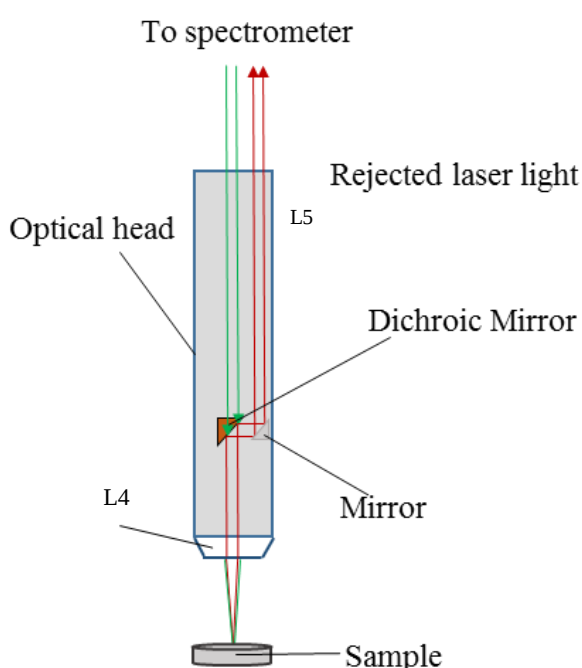


Figure 3.10: A schematic of the M-10X optical head in an in situ instrument configuration.

scattered light is collected. Light scattered by the sample is immediately intercepted by the optical probe. It is then filtered and routed to the optical fibre as described in Section 3.1.2.

3.1.4 SPECTROGRAPH

Two separate spectrographs have been used for this study. The first was a Kaiser Optical HoloSpec, f/1.8 spectrograph. This is the spectrograph integrated into the ExoMars RLS prototype system (for a full description of RLS see Section 1.3.4 in Chapter 1). This spectrograph is 30 x 20 x 25cm and contains a collimating lens, a transmission diffraction grating and a camera lens. The entrance slit is circular and is 100 μ m in diameter (i.e. the exit aperture of the coupling optical fibre). The collimator is a single compound lens with a focal length of 85mm and a 58.5mm diameter. At a (fixed) 45 degree angle is a HoloPlex HPG-532, holographic transmission grating. The grating is 66 x 72mm in size and disperses collimated light into two diffraction orders; the first covering 175cm⁻¹ to 2250cm⁻¹ and the second covering 2000cm⁻¹ to 4400cm⁻¹. The grating has 6000 grooves/mm, resulting in a grating resolution of 3cm⁻¹. The camera lens is located at a 45° angle from the diffraction grating at a distance of 7cm (which can be altered depending on the spectral range required at the detector plane). The compound lens is

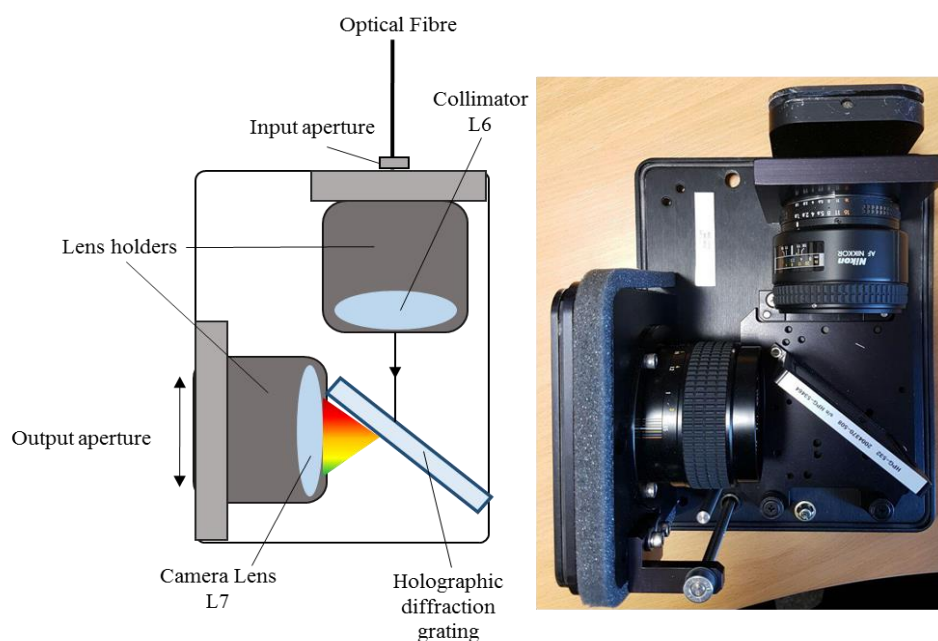


Figure 3.11: A schematic and photograph of the Kaiser Optical HoloSpec spectrograph.

58.5mm in diameter with a focal length of 85mm. A schematic of the spectrograph is provided in Figure 3.11.

A second spectrograph was specifically developed in order to optimise the throughput of a Raman instrument, i.e. to maximise the amount of light transferred from the collection optics to the detector. The layout of the spectrograph is shown in Figure 3.12. The system uses a 2.5cm diameter BK7 lens to collimate the incoming light from the optical fibre. The light is then dispersed by a 12.7x12.7mm transmission grating (with 600 grooves/mm in Schott B270 material) into a single diffraction order ranging from 0- 2000 cm^{-1} . The grating has a theoretical transmission efficiency of ~50-60% within the 500-600nm wavelength range. The camera lens was 2.5cm in diameter and had a focal length of 5cm. The detector was placed at distance of 5cm from the lens (using a 50 mm motorized translation stage stage). The transmission efficiency of both the collimating and camera lenses was 99.5%.

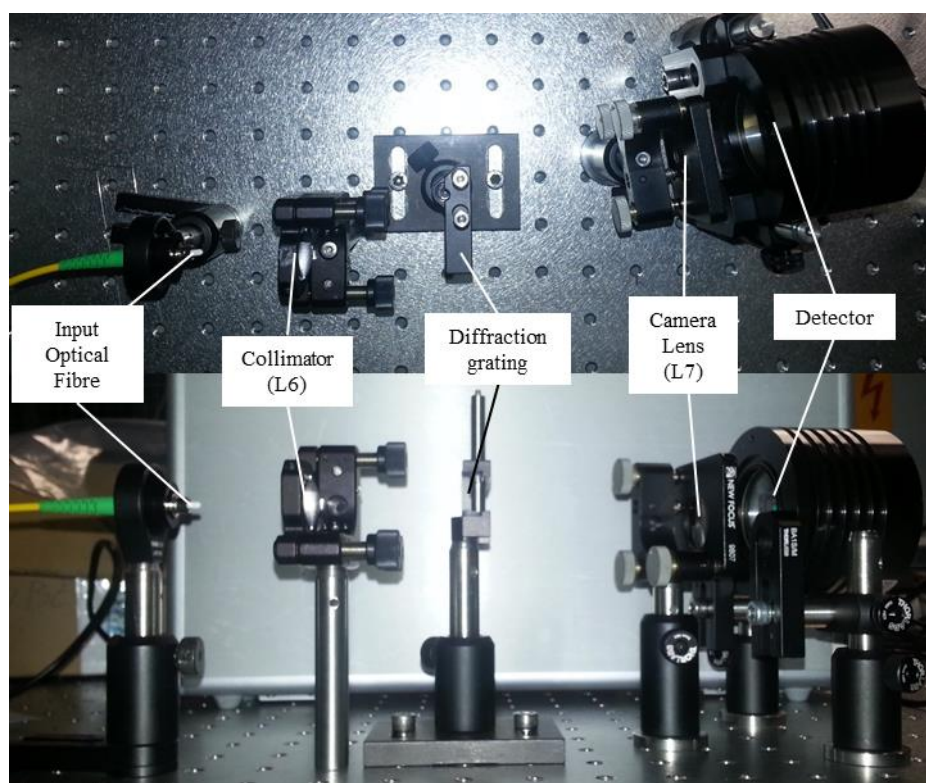


Figure 3.12: A spectrometer designed and developed as part of the study to maximise throughput of the Raman Spectrometer system.

3.1.5 DETECTOR

Four different detector systems were used for this study. Each device was mounted on a moveable platform (to facilitate optimum focusing) located at the focal point of the camera lens used for a particular spectrograph. For all instrument configurations and environments, the detectors were shielded from ambient light using enclosures and optical blocking cloth. The key properties of each of the detectors used in this project are listed in Table 2.5.

The first detector used in this project was a Commercial Off The Shelf (COTS) astronomy camera, SXVR-H9 USB2, manufactured by Starlight Express Ltd (Figure 3.13). The camera uses a Sony ICX285AL, Exview interline imager; a 1392 x 1040 pixel full-frame CCD, with an electronics shutter. The CCD is cooled via a fan assisted thermoelectric cooler which is incorporated within the SXVR-H9 USB2 enclosure, along with the associated drive and read-out electronics. This detector was used to acquire data from instrument configurations 1, 2, 4 and 5.

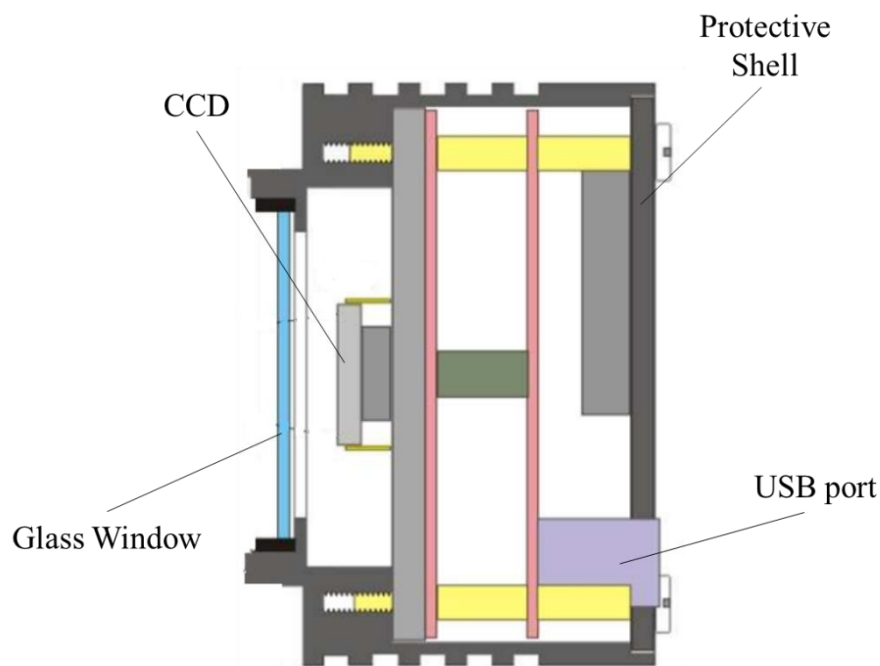


Figure 3.13: A diagram of the SXVR-H9 USB2 camera, adapted from (Hattey, 2009).

The second camera was a bespoke CCD230-42 (manufactured by e2v Technologies) based system. The device contains 2048 x 2064 pixels that can be read out via (up to) four output nodes. The CCD is located in a 7cm x 5cm proximity board, which provides local signal filtering and variable off-chip gain (within the 3-9 range), so that the dynamic

range can be optimised according to the requirements of each experiment. The proximity board also includes an AD9814 CDS/analogue to digital converter mixed signal ASIC which performs CDS on the CCD output signal (see Chapter 2 Section 2.2.1 for a detailed description of CDS techniques). The detector drive electronics and FPGA board are connected to the proximity board via cables which can extend to distances of one metre or more, with a USB or Gigabit Ethernet interface to the host computer.

A CCD47-20 (a frame transfer device) based camera was also used during these studies. The Peltier packaged device (manufactured by e2v technologies) is provided with an integrated, 2 stage thermoelectric cooler. The chip contains two on-board temperature sensors, which can be monitored using the software interface developed for this study (described in Section 5.1) in order to provide direct feedback to the TEC drive electronics. In principle, the enclosure can be coupled to a water cooled heat sink in order to achieve operating temperatures of around -50°C . Similarly to the CCD230 based system, this device is connected to a proximity board, 7cm x 8cm in size, which provides local signal filtering, an off-chip gain of 6 and CDS/digitisation. Both the CCD47-20 and the CCD230-42 systems were used as part of configurations 1, 2, 4 and 5 and were operated at room temperature.

Finally, The PI-MAX4 manufactured by Princeton Instruments was also used for these studies. It is a fully integrated ICCD camera, capable of pico-second gating through a variable, high voltage microchannel plate. The detector is a CCD30-11 which has a 1024x256 pixel format. The system is cooled by an integrated TEC with an air-heat exchanger. The camera is controlled by the Princeton Light Field software via a Gigabit Ethernet interface in order to enable rapid data retrieval. The Light Field software was used to optimise the ICCD and retrieve data in experimental configurations 3 and 6. Data acquisition was triggered by an external pulse from the laser and sequenced using the timing diagrams within the software interface (further details are provided in Chapter 5).

3.1.6 DETECTOR CONTROL SOFTWARE AND SPECTRUM ACQUISITION

Images were acquired from the COTS SXVR-H9 USB2 camera using the SXV_Hmf_USB Imager processing software V-3.9d (Figure 3.14). The software provided control over the integration time, number of acquired frames and on-chip binning. The software also provided a method for background image subtraction (the subtraction of an image that represents the level of ambient light incident on the detector). Figure 3.14 also contains an example CCD image acquired using the SXVR-H9 USB2 camera.

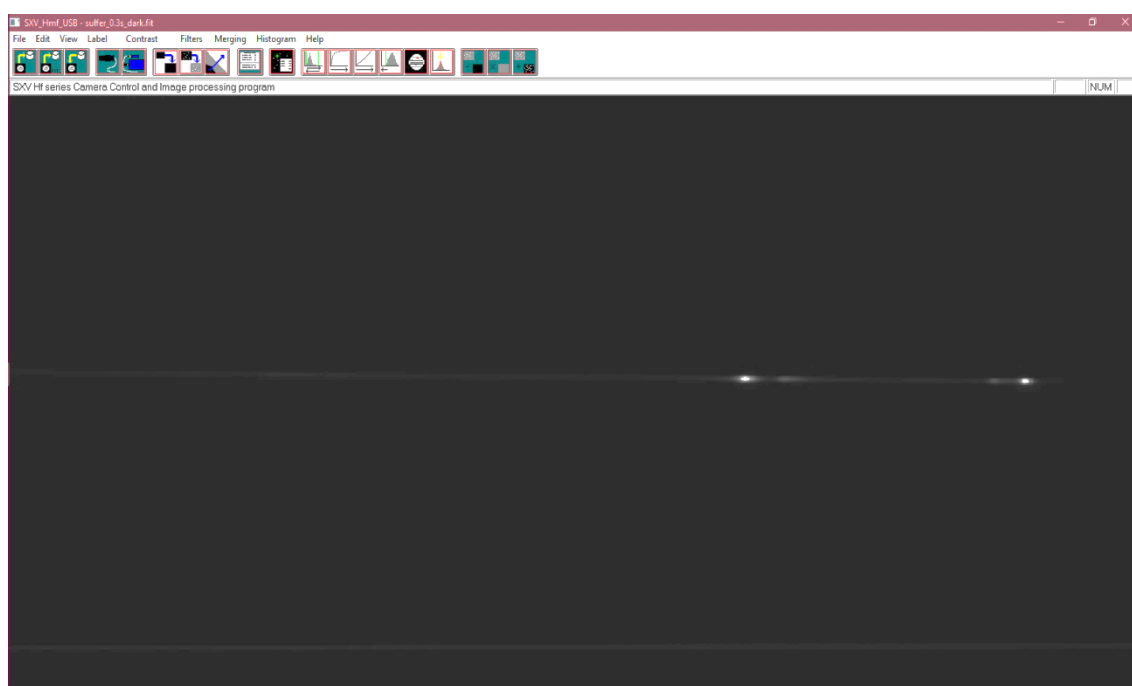


Figure 3.14: A CCD image acquired using the SXVR-H9 USB2 camera software. Two diffraction orders can be seen, with the upper order containing Raman spectra features from a sulphur sample.

Spectra were extracted by summing the intensity of the pixels within each column that contain a spectral signal. The intensity of each binned column is plotted against the column number. Figure 3.15 shows a spectrum extracted from the CCD image in Figure 3.14. The optimisation of this data extraction process is described in Chapter 5, Section 2.5.

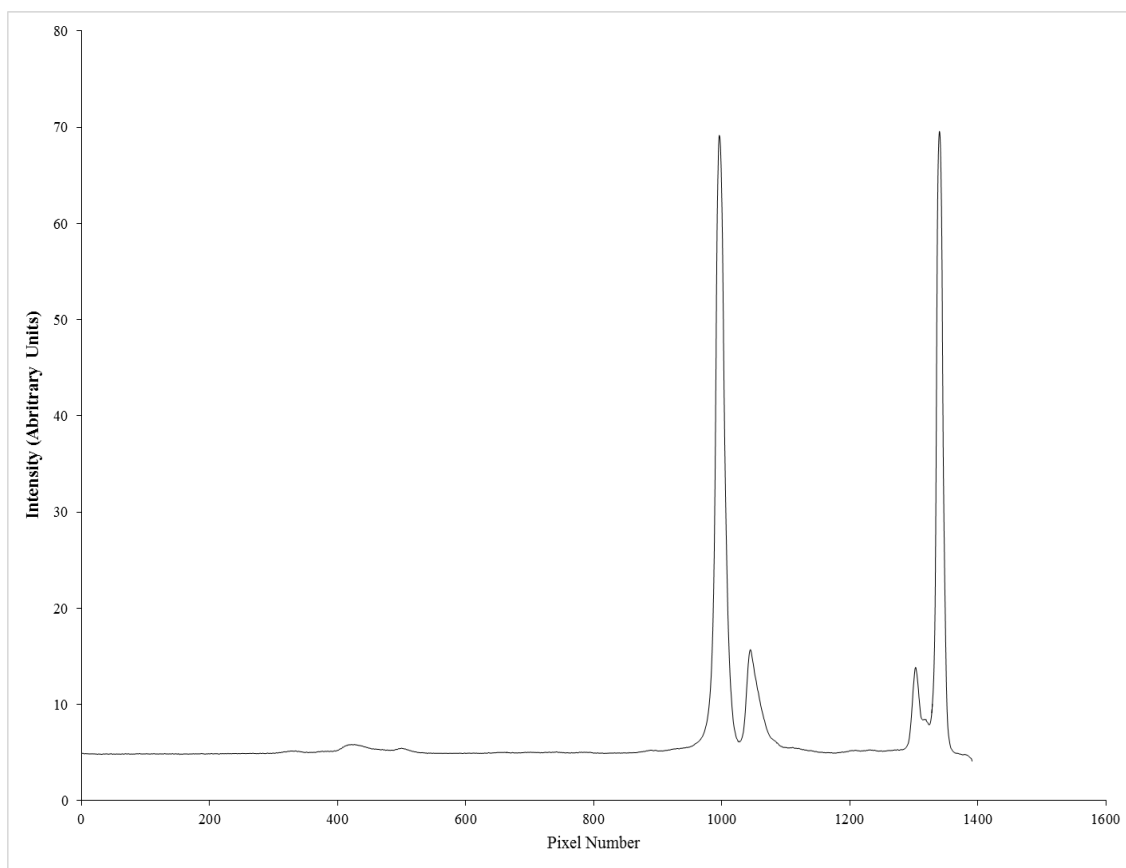


Figure 3.15: A spectrum extracted from the CCD image in Figure 3.14.

Spectra were obtained from the Princeton Instruments' PI-Max4 camera using a Princeton Light Field software application (Figure 3.16). The Princeton Light Field software provided a method of altering CCD acquisition parameters, such as integration time and the number of frames as well as the gain and gate width of the multichannel plate. The software also provided post processing tools such as background image subtraction and image stacking. Spectra were extracted from acquired images by summing the pixel intensities for individual columns (selected by a user defined region of interest) that contained the spectral order.

The e2v detectors described in section 3.1.4 were operated using the Instrument Control Software (ICE) an application developed during this study. Data collection from these devices was also facilitated by the same software interface. A full description of the software interface and its functionality is given in Section 5.1.

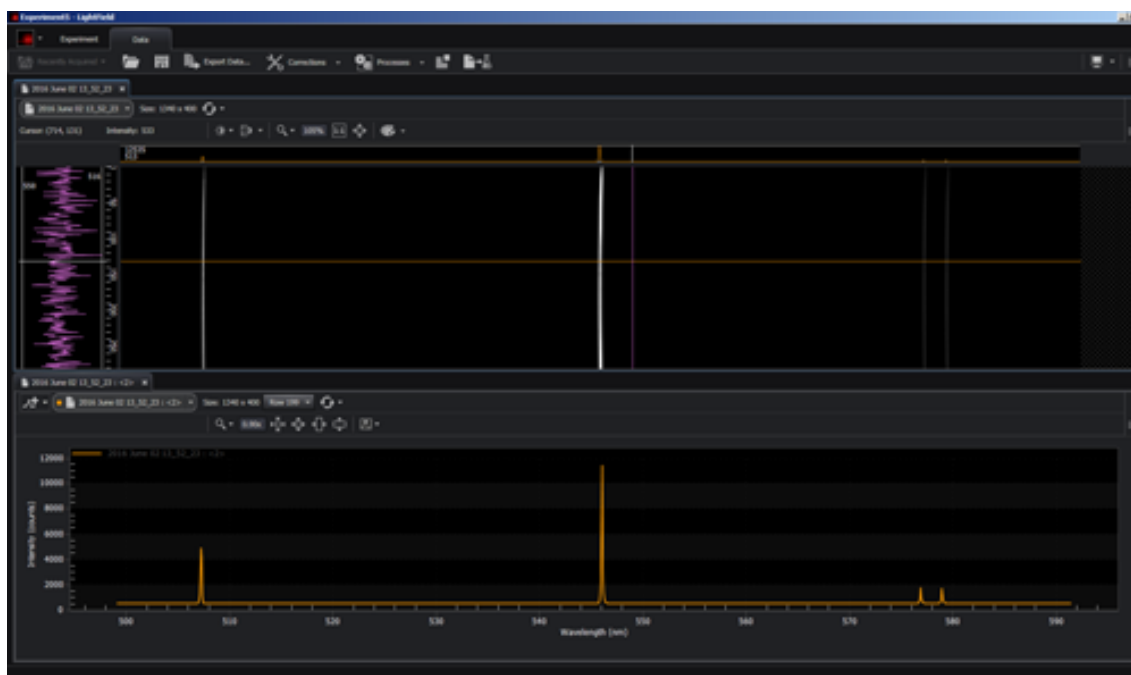


Figure 3.16: A screenshot of Princeton Instruments' Princeton Light Field software.

3.1.7 SPECTRAL CALIBRATION

The spectral calibration of a Raman instrument defines the relationship between the wavelength (and wavenumber) of a scattered photon and the position on the CCD at which it is detected (i.e. the pixel position). The calibration process consists of obtaining

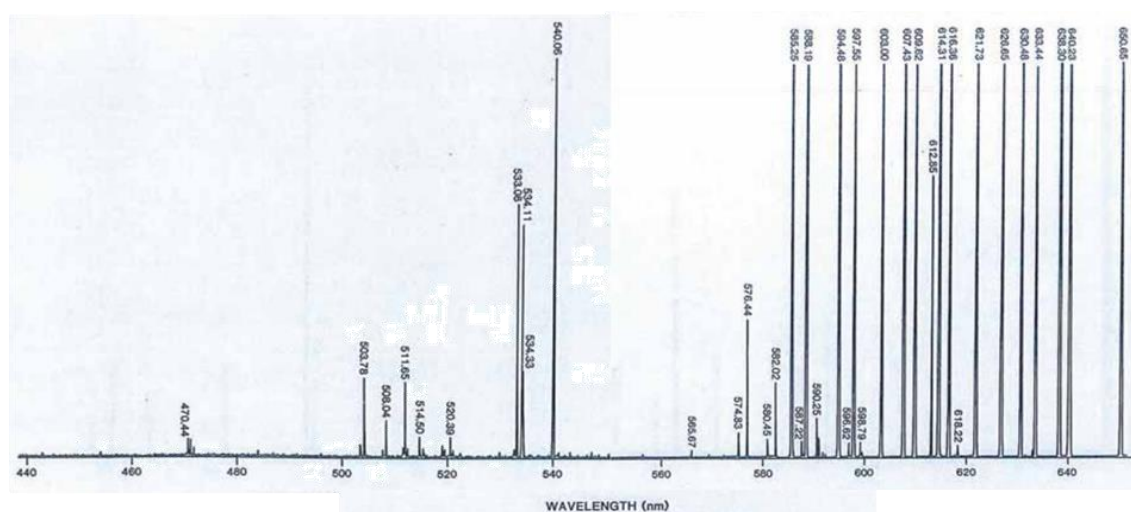


Figure 3.17: A typical neon spectrum obtained from a neon calibration lamp. Credit: Newport Corporation

a spectrum from a standard calibration source, of which the emission properties (such as wavelength and intensity) are well known and then accurately determining the position of each band on the surface of the detector. An ideal calibration source for a Raman instrument emits many discrete emission bands spanning over the entire detectable wavelength range of the instrument. Figure 3.17 shows the emission spectrum of a Neon discharge lamp, a commonly used calibration source for this purpose. To comprehensively calibrate an instrument, spectra are obtained from the standard source while the instrument is in a configuration representative of that used to acquire subsequent scientific data. Once spectra are acquired, wavelengths (or wavenumbers) of the emission bands (which are well documented (Oriol Instruments, 2016)) are used, along with the pixel positions, to calibrate the instrument. Often it is necessary to repeat the calibration process several times during experimental procedures as a consequence of unintended movement or environmental changes (such as temperature fluctuations).

As part of the Raman instrument development, a two stage calibration process was incorporated into the ICE interface. This section describes the algorithms developed to perform an accurate and reliable spectral calibration for the Raman instrument. The first stage determines the relationship between the pixel position of a photon and its

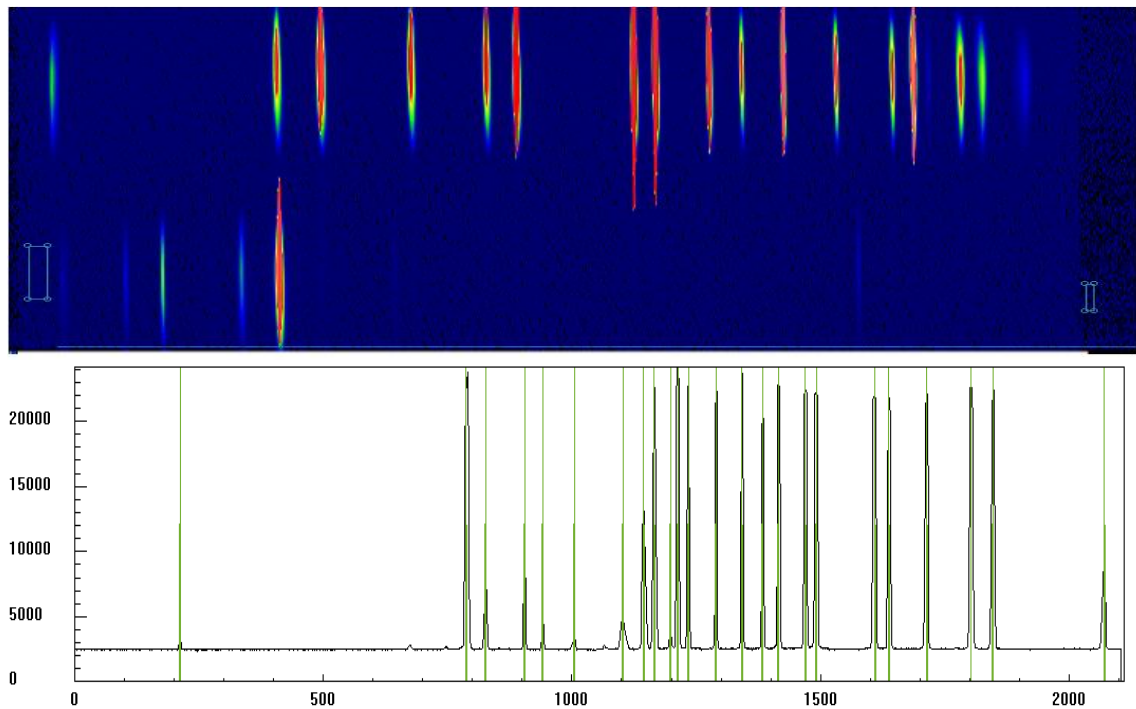


Figure 3.18: A neon spectrum obtained for the calibration process. Since the instrument is uncalibrated the intensity is plotted in terms of detector pixels, not wavenumber. The noise is defined as the standard deviation in the data within a region not containing an emission band (highlighted above).

wavelength and the second stage determines the relationship between pixel position and wavenumber using knowledge of the instrument's laser wavelength.

The first stage of the calibration process involves acquiring a spectrum from a Neon calibration source. Algorithms within the software autonomously identify bands within the neon spectrum by assessing each data point (pixel) in turn. A pixel is assumed to contain a peak if its intensity is above a user set threshold of n standard deviations above the noise level. The noise level is calculated using user defined regions in the image that only contain background signal/electronics noise (see Figure 3.18).

In addition to checking that an individual pixel exceeds the noise threshold, the software also checks that the pixel value is a local maximum (i.e. exhibits a signal level that is larger than the 4 pixels immediately surrounding it).

To maximise the reliability of the calibration process, the pixel to wavelength calculation should be based on high intensity peaks with unambiguous pixel positions. Consequently, an additional algorithm was incorporated to ensure that the most intense peaks were not

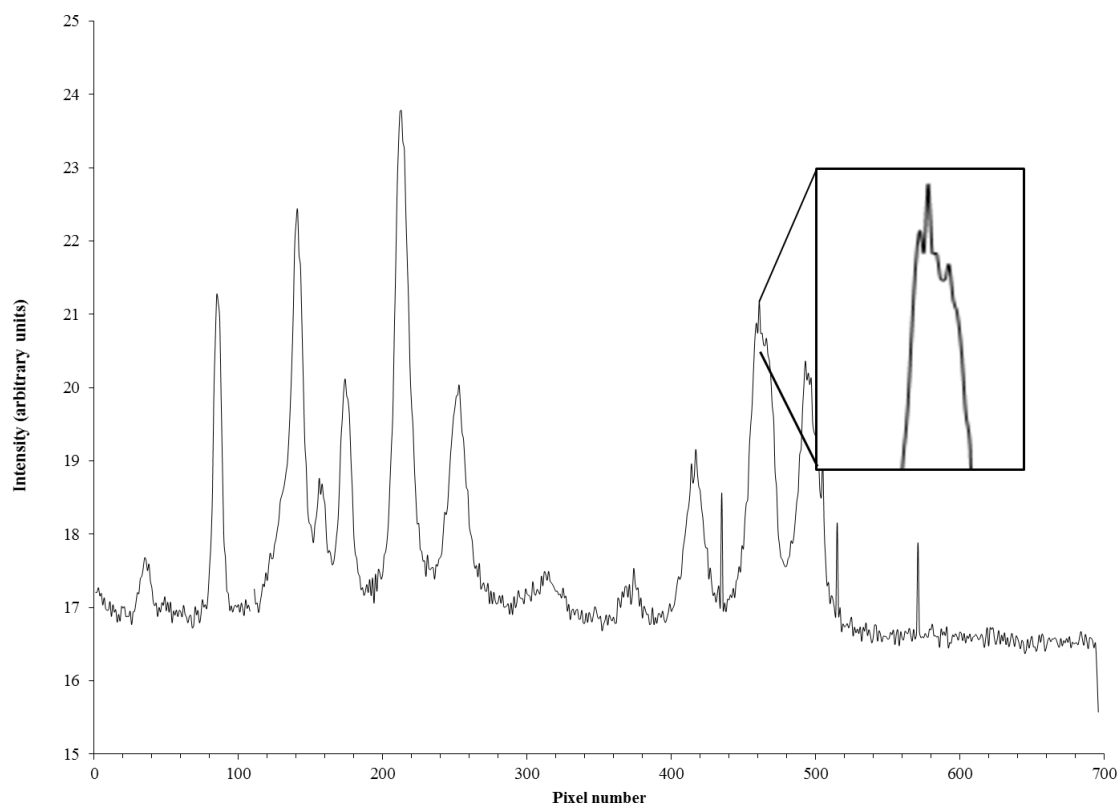


Figure 3.19: A Raman spectrum acquired from a sample of paracetamol that shows the effects of noise on band definition. The inset shows a close up of an intense band, the maximum position of which is ambiguous due to the irregular fluctuations in the signal (noise).

identified multiple times due to the presence of many local maxima in a band (possibly caused by noise). This effect is illustrated in by Figure 3.19.

To achieve this, the pixels were ordered in terms of their intensity. Starting with the most intense pixel, the software determines if the pixel was previously flagged as containing a band. If the pixel does contain a band, the software subsequently determines if the surrounding pixels (within a defined window) were also flagged as containing peaks. If multiple close pixels do contain emission bands, then it is likely that they are all part of the same emission band and that they are local maxima caused by noise (this effect can be seen in the insert featured in Figure 3.19). If the surrounding pixels have been flagged as maxima then the central peak is considered to represent the actual position of the peak. As stated earlier, it is important to perform the pixel to wavelength calculation using as many known emission bands as possible, distributed across the full detectable wavelength range, in order to achieve an accurate calibration. However, if this additional processing significantly reduces the overall number of bands identified, then the governing parameters (such as the noise threshold and defined flag window) should be changed and the process should be repeated until a sufficient number of peaks have been identified. Section 5.1 shows how the ICE software was developed to facilitate the process described here.

To calculate the optimum relationship between the pixel position of the detected emission bands and their wavelengths, the software first compares the identified bands to known theoretical emission bands in order to assign them a wavelength. To achieve this, the software chooses two peaks from the theoretical list (preferably at either end of the diffraction order). The software then chooses the pixel positions of two flagged peaks in the diffraction order and temporarily associates them with the theoretical wavelengths. A conversion factor is then calculated by dividing the distance between the peaks (in pixels) by the change in wavelength. This gives a pixel/wavelength correlation factor. Using this conversion factor, pixel values are calculated for each of the theoretical wavelengths in the list. These predicted band positions are then compared to the identified positions of the emission bands and the closest match to each is identified. If each predicted band is matched to a different identified band (i.e. a predicted band is not matched to two identified bands simultaneously), then a least squares polynomial fit is performed on the identified peak positions and their associated theoretical wavelengths. The polynomial coefficients are then used to calculate the wavelength for each of the identified pixel

positions. The wavelength values of the detected emission bands are compared with the theoretically matched ones. This is achieved by calculating the RMS of the differences between each wavelength of each identified band and the associated theoretical band. The RMS value is then used to assess and optimise the polynomial order used for the calculation.

The matching process described here is repeated for all combinations of the initial match (between the two theoretical bands and the two chosen identified bands of neon), to find the optimum combination that provides the smallest RMS value and therefore the best global fit between theoretical and calculated wavelengths, based on their pixel positions. The most accurately matched wavelengths are used in the final stage of the calibration.

The second stage of the calibration process calculates the wavenumber off-sets, using a Raman spectrum from a material such as paracetamol or cyclohexane- a material with many strong Raman bands, distributed across the full spectral range of the instrument. The bands are identified using the process described above: i.e. using a user defined noise threshold, n , and window to find local maxima within the spectrum.

Once a sufficient number of bands within the Raman spectrum have been flagged by the identification algorithms, the software determines an optimal polynomial to convert the pixel position of a band to a wavenumber off-set. As before, the creation of a polynomial is repeated many times using all combinations of the two initially associated pixel positions and theoretical wavenumber bands. Each time the polynomial is used to calculate a wavelength for each band which is then compared to the theoretical band. The similarities between the calculated and theoretical wavelength are assessed using the RMS value of the differences between them. The RMS values are again used to assess and compare the accuracy of the polynomial and therefore the conversion from pixel position to wavenumber.

The final stage of the calibration process compares the pixel-to-wavelength relationship derived from the previous two stages to assess whether both calibration stages provide a similar pixel-to-wavelength conversion, i.e. there has been no mechanical shift within the instrument between switching sources. Figure 3.20 shows two examples of the calibration stage comparison. The blue points are derived from the first stage of the calibration process, while the red points are generated in the second stage. By plotting the two conversions, the accuracy of the two stages can be compared and assessed.

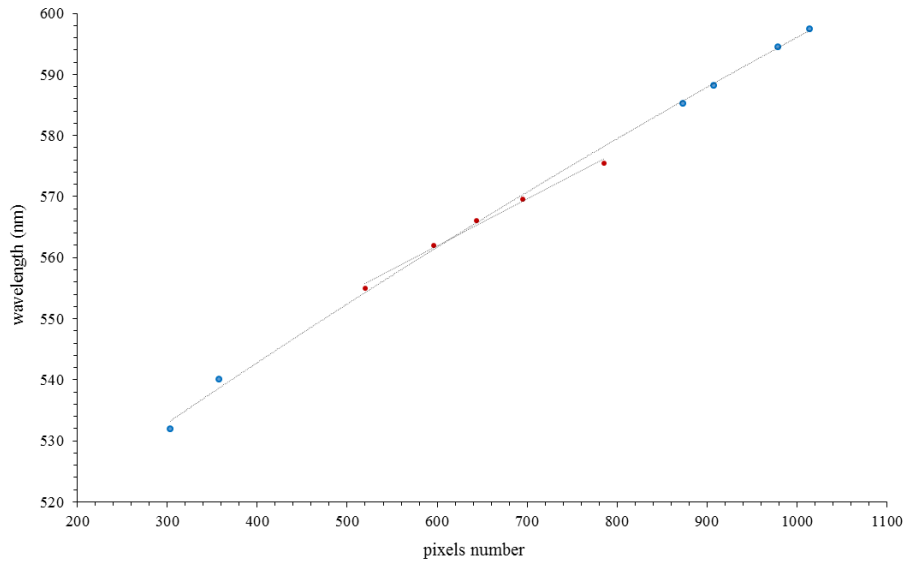


Figure 3.20: A pixel to wavelength relationship plot. The plot features relationships derived in the neon stage as well as the Raman spectrum stage of the calibration process.

Since the two stages align reasonably well in this case, any two peaks featured in the plot can be used to calculate an actual laser wavelength for the instrument using Equation 3.1.

$$\left(\frac{1}{\lambda_{laser}} - \frac{1}{\lambda_{band}} \right) \times \frac{1}{100} = \text{wavenumber offset} \quad 3.1$$

where λ_{laser} is the wavelength of the laser in nm and λ_{band} is the wavelength of the vibration mode in nm. The wavenumber offset has the unit's cm^{-1} .

3.2 THE RADIOMETRIC MODEL

3.2.1 OVERVIEW

The radiometric model uses a number of different algorithms to describe the passage of light from the input of the instrument to the output in order to quantify the overall instrument performance. The model accounts for all aspects of performance including the efficiency of the collection optics (in terms of transmission and alignment geometry), spectrograph input/output optics and diffraction grating, as well as laser power and working distance to the sample. In addition, the model also considers the fundamental detector properties and operating modes. It also takes into account noise factors such as ambient light, fluorescence and dark current. In its entirety, the model can be used to simulate separate instrument configurations and specific operating conditions and scenarios (environments) in order to assess the basic feasibility and theoretical performance to be anticipated for a particular experiment.

The model incorporates several different component elements, each representing a different subsystem within the instrument, i.e. the laser and output optics, the sample response, the collection optics, the spectrometer, the detector and the post processing performed on the data. Each of these components is described in detail below, along with a discussion of the origin and properties of photons as they enter and leave each subsystem. Each section also includes a description of the input parameters (that describe a component or the signal at that stage in the instrument), the algorithms (the calculations performed to change the signal or noise levels to simulate real phenomena occurring within the instrument that affect how light behaves) and the model outputs. The layout of the simulation is described by the flowchart in Figure 3.21. Many outputs are used in subsequent sections since a lot of the parameters interrelate and effect several aspects of the instrument performance at once. The model ultimately determines a theoretical signal-to-noise ratio for a given configuration or experimental situation which can be used to quantify the instrument's performance.

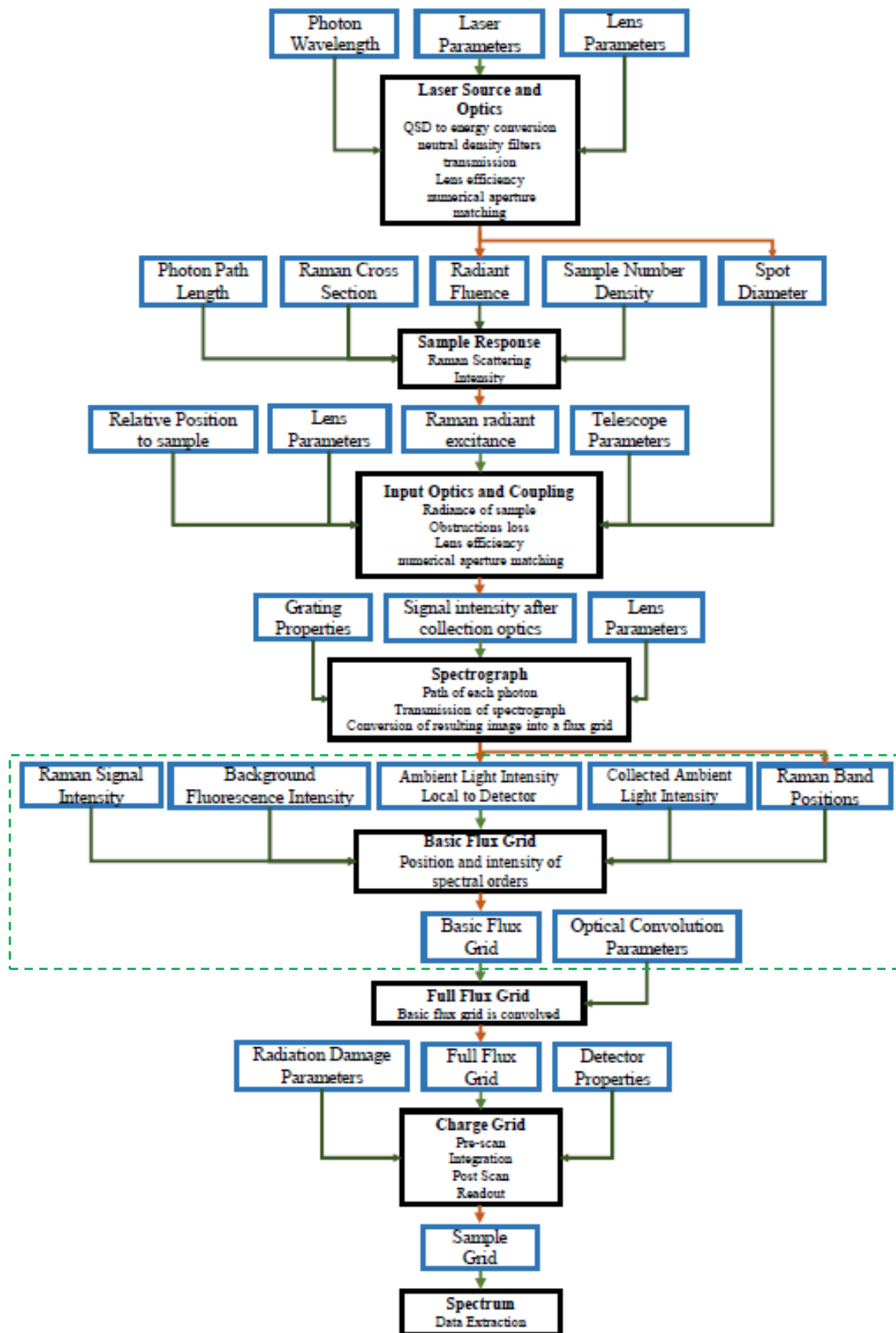


Figure 3.21: A flow chart describing the sequence of algorithms used in the radiometric model. The green box indicates the algorithms that feature in both the radiometric model and the software simulation, that create an overlap between the two optimisation tools.

3.2.2 LASER OPTICS

This part of the model determines the resultant energy per pulse and the laser spot size at a given working distance and hence the excitation energy density at the sample. To do this the model requires several fundamental laser parameters, such as the wavelength of the emitted photons, the number of pulses produced in a second (the pulse repetition rate) and the average width of a pulse. These parameters are specified in Section 3.1.2. The energy per pulse is also required. It represents the total optical power integrated over the duration of a pulse (pulse width). Figure 3.22 gives an example of how the laser pulse power varies with time.

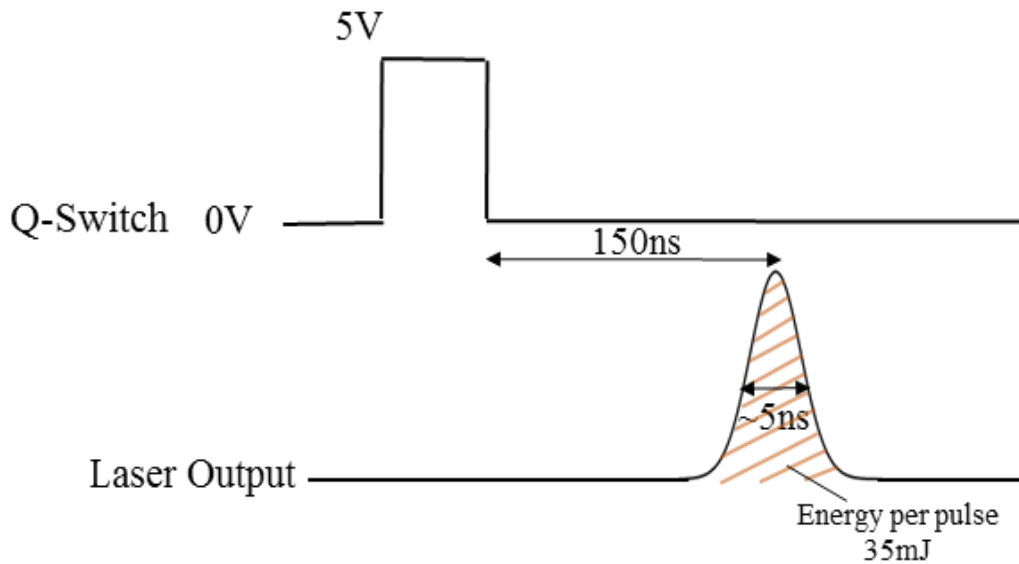


Figure 3.22: An example of a laser pulse profile.

The energy of a laser pulse is obtained by implementing a particular Q-switch delay. The relationship between the Q-switch delay and the energy per pulse is given in the subsequent section. The model also calculates the laser energy provided by a system that utilises a continuous laser, using the power stated in Section 3.1.2.

In order to derive an energy density, it is necessary to consider the beam diameter at the sample. Assuming that the laser output has a Gaussian profile the diameter of a laser is defined as the point on the x-axis where the intensity falls to $1/e^2$ (~ 0.13) of the intensity at $x=0$, i.e. the centre of the laser beam. The beam diameter can be altered by optically focusing the beam using lenses, however there will be a lower limit to the beam diameter as it becomes diffraction limited. In addition, if the beam is un-collimated, it will naturally

diverge over a given distance therefore the beam diameter will be larger the further away from the laser aperture (cavity exit) it is. The laser divergence is a known property of the laser and typically depends on the laser type (i.e. the method with which the light is produced) and the wavelength of the emitted photons.

The laser energy is attenuated by the optical components that redirect and focus the laser light onto the sample. Lenses have several important parameters that effect the throughput of the system: the lens diameter, focal length and transmission efficiency. The diameter and the focal length impact on a lens's ability to collect light. A larger lens will intercept more light from a given source than a smaller lens i.e. it will define a larger solid angle (see Figure 3.23). The focal length of a lens is defined as the distance between the focused image produced by the lens and the lens itself. It can also be defined as the distance at which collimated rays are brought to a focused point. Similar to the lens diameter, the focal length of a lens has an impact on the collection power of the lens (see Figure 3.23) as it also defines the solid angle from which light is collected from the source.

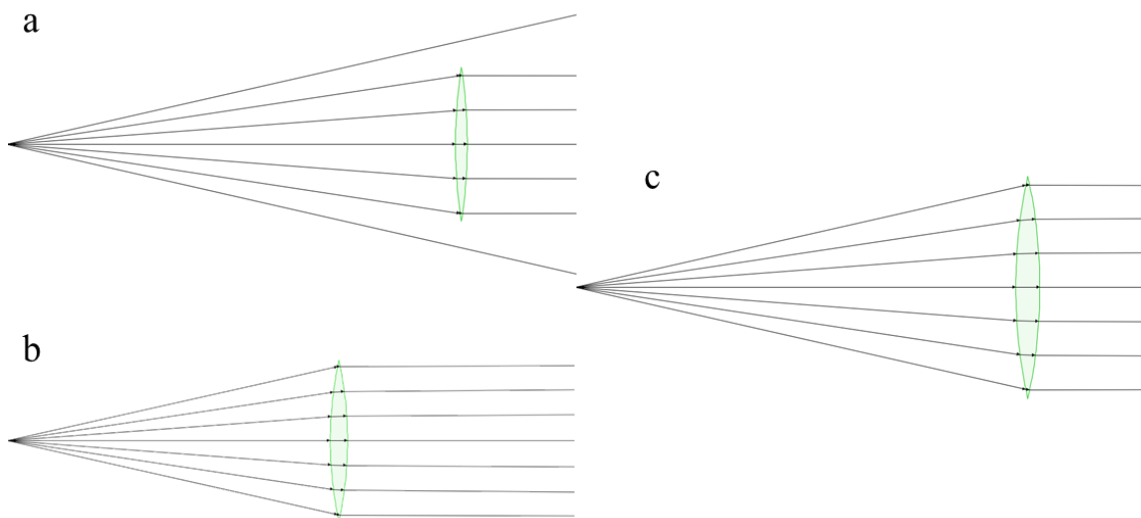


Figure 3.23: A diagram illustrating the effects of increasing the diameter and decreasing the focal length of a lens. (a) Shows a biconvex lens and the number of light rays it intersects with represents the collection power of the lens. (b) shows that the number of rays intersecting the lens increase if the focal length of the lens is decreased and (c) shows that the collection power of the lens increased as the diameter of the lens is increased.

The transmission efficiency of a lens describes its ability to transmit light. Depending on the material that the lens is composed of, a fraction of the incident light will be absorbed and reflected. Consequently, lenses are often coated with anti-reflection coatings (see

Section 2.1.2 for specific details) in order to increase the amount of light that ultimately passes through the lens.

The model also accounts for the attenuation of neutral density (ND) filters. ND filters are used during the focussing and alignment stages to reduce optical power (or intensity) of light incident on the sample. The fraction of the optical power transmitted is described in terms of the optical density. The ND filters used in this experiment range from 0.1 to 5 in optical density (providing a throughput range of 77% to 1.0×10^{-6} %).

MODELLING LASER SYSTEM PROCESSES

The initial number of photons in the system is determined by the energy per pulse supplied by the laser. The pulse energy of the laser is controlled by the Q-switch delay (in μs). The required pulse power can be converted to a Q-switch delay using Equation 3.2:

$$QSD = 0.46E + 104.98 \quad 3.2$$

where E is the energy per pulse (mJ) that is required for the experiment. In this case E is 35mJ per pulse. On exit from the laser head, the light enters the beam separator which redirects any photons which do not have a wavelength of 532nm. This is achieved using dichroic filters and lenses. Equation 3.2 accounts for the loss in laser light intensity due to the imperfect transmission and reflection of these filters and mirrors (i.e. the equation calculates a Q-switch delay that is required to obtain a specific pulse energy at the exit of the separator).

Irrespective of the type of laser (pulsed or continuous) the excitation is then focused by a lens (L1). The fundamental properties of a lens are usually described by a parameter called the numerical aperture. The numerical aperture of the lens is a unitless measure of a lenses ability to collect light by defining the range of angles over which light can enter the lens and is given by Equation 3.3.

$$NA = nD/2f \quad 3.3$$

where n is the refractive index of the surrounding medium (e.g. the refractive index of air is ~ 1), D is the lens diameter (in metres) and f is the focal length in metres. To maximize the amount of light collected by any given lens, the lens NA should be matched to or larger than that of a light source (in this case, the laser beam), i.e. the light cone from the laser (created by the natural divergence of the light) should not subtend an angle greater than the maximum collection angle of the lens otherwise photons will be lost from the system (see Figure 3.23). The actual amount of light lost from a system with mismatched optics can be calculated using the ratio of the two numerical apertures.

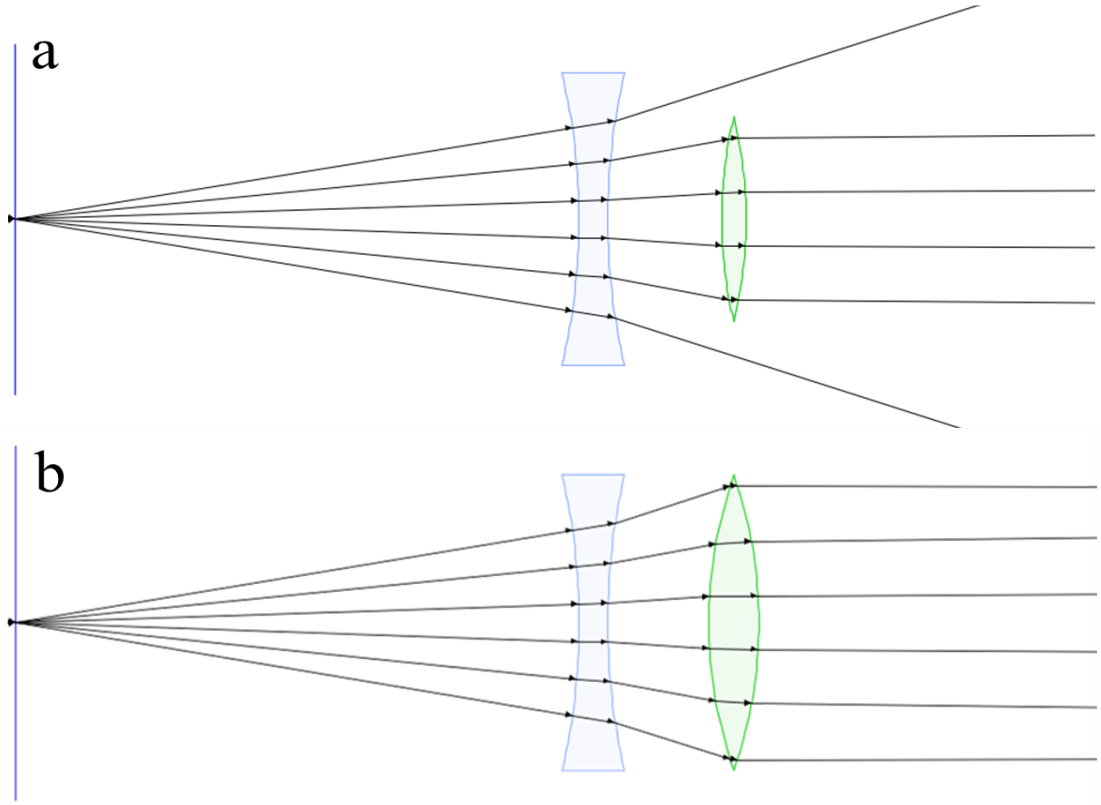


Figure 3.24: An example of numerical aperture matching to optimise the collecting power of the optical system. (a) shows an example of when the numerical apertures are not matched and (b) shows how the apertures can be matched, in this case, by increasing the diameter of the second lens.

For example, in order to optimally focus the excitation source onto a sample, the beam must first be collimated. This is achieved by placing the excitation source just beyond the focal point of L1 in order to match the numerical apertures. The collimated beam is then focused using a second lens (L2), to maximise the energy density at the sample. Due to the diffraction limit of a Gaussian beam, a focused laser beam has a minimum spot size, which will occur at the focal point of the second lens. The minimum spot size is known as the ‘waist’ and is given by Equation 3.4

$$\omega_o = \frac{2f\lambda}{\pi D} \quad 3.4$$

where ω_o is the minimum spot size, f is the focal length of L2, λ is the wavelength of the laser light and D is the diameter of the lens. All parameters are in units of metres. To extend the focal point of the system (i.e. focus the laser at a distance much greater than

the focal length of L2) a compound lens is used. The resulting focal length and hence the distance at which the laser is focused is given by Equation 3.5,

$$\frac{1}{F} = \frac{1}{f_1} + \frac{1}{f_2} \quad 3.5$$

where F is the resultant focal length in metres, f_1 is the focal length of the first lens and f_2 is the focal length of the second lens. This equation can be extended to calculate the focal length of a compound lens containing n individual lenses. The resultant focal length can be altered to match the distance to the sample, but in turn will affect the collection power of the system.

For alignment practicality, the laser intensity was reduced using ND filters (see Section 3.2.2). The percentage of incident light transmitted by the ND filters is given by Equation 3.6,

$$\% \text{ of light transmitted} = \frac{I}{I_0} * 100 = 10^{-d} * 100 \quad 3.6$$

where I is the intensity (energy per pulse or pulse power) after transmission, I_0 is the incident intensity and d is the optical density of the filter. The optical density of the filters range from 0.1 to 4 and can be added together in order to decrease the overall percentage of light transmitted.

Assuming all numerical apertures have been matched and no photons have been lost due to misalignment, the transmission loss can be calculated for the entire optical system. Equation 3.7 uses the transmission efficiencies of the two lenses to calculate the laser energy per pulse at the sample,

$$E_{sample} = E_0 T_{L1} T_{L2} \quad 3.7$$

where E_{sample} is the energy per pulse at the sample, E_0 is the energy per pulse on exit from the separator and T_{L1} and T_{L2} are the transmission efficiencies (not as a percentage) of L1 and L2 respectively. Using the theoretical spot size and energy per pulse at the sample, Equation 3.8 calculates an energy density (radiant fluence, H_e) with units of Jm^{-2} ,

$$H_e = \frac{E_0}{\omega_0} \quad 3.8$$

Equation 3.8 gives the energy density at the sample for a single laser pulse. To compare the total energy delivered to the sample by each laser (pulsed and continuous) it is necessary to calculate the energy delivered to the sample by both options in one second. For a pulsed laser with a constant repetition rate, the energy delivered in one second is given by Equation 3.9,

$$I = H_e R \quad 3.9$$

where I is the irradiance (in Wm^{-2}) of the laser and R is the repetition rate, which is 10Hz for the Surelite I-10 laser.

Consequently, the ratio between the power delivered to the sample by a pulsed laser and the power delivered by a continuous laser in one second is given by Equation 3.10,

$$Ratio = \frac{H_e R}{P} \quad 3.10$$

where P is the power per unit metre squared of the continuous laser.

This section calculates the numerical apertures for each lens in the output optical system. The NA of a lens must be equal to or larger than that of the source. This also includes the NA's of multiple lenses. If the numerical apertures of the lenses are not matched, light will be lost from the system. The amount of light lost is obtained from the ratio of the NA's.

The radiometric model also derived a minimum laser spot diameter (i.e. the diffraction limit, ω_0 , of the laser using various lenses). Using the minimum spot size, the model calculated the maximum radiant fluence (energy per unit area) for both a pulsed and continuous laser systems using their corresponding laser energies. Finally, this section gives a ratio of irradiances (Wm^{-2}) in order to compare the amount of energy (and therefore the quantity of 532nm photons) delivered to the sample in a given amount of time for both the pulsed and the continuous lasers.

3.2.3 SAMPLE RESPONSE

There are many factors that influence how many photons reach the instrument once a sample has been excited by the incident radiation. The laser wavelength, the polarizability of a molecule and the temperature of the sample are all factors that affect the probability of an incident photon being Raman scattered by the molecules in a sample. In order to fully calculate this probability, a full quantum mechanical analysis would be required which is beyond the scope of this study. However, this section of the model uses a well referenced and thoroughly tested top level mathematical description of the sample response to the laser excitation in order to calculate a theoretical Raman scattering power or the number of Raman photons per second being emitted by a sample (McCreery, 2005).

The number of scattered photons depends on several material properties of the sample, such as the model requires the number density, N , of a sample. This is defined as the number of molecules within a given volume. This will be specific to the nature of a particular material, for example the values of N for water and diamond are 33.3×10^{27} and $176.2 \times 10^{27} \text{ m}^{-3}$ respectively. The model also uses the path length of the laser photons, which is defined as the distance from the sample surface to the location in the material where the scattering of incident light is likely to occur. Depending on the experiment, the path length can be defined in a number of ways, such as, the depth of focus of the laser or sample thickness. If the sample is a strong absorber then the path length may be defined as the absorption path length (which depends on the absorption coefficients of the materials in a specific sample). The path length is usually around $\sim 1\text{mm}$, but for metallic (highly absorbing) samples the path length may be as low as 100nm .

The number of photons that contribute to the inelastic scattering is also governed by a sample property known as the integrated Raman scattering cross section. The integrated Raman scattering cross section is defined as the quantified probability of an incident photon inelastically scattering with a molecule. The scattered light will have shifted in frequency (compared to the incident laser light) as some of the photon energy will have been used to promote the molecule into a particular mode. The frequency of the resultant photon is known as the mode frequency. The Raman cross section of a molecule is proportional to a particular vibration mode frequency, as well as the excitation wavelength and the polarizability of the molecule. The Raman cross section has the unit $\text{cm}^2 \text{ molecule}^{-1} \text{ sr}^{-1}$ and has a magnitude in the range 10^{-8} to 10^{-30} depending on how strong

or weak the Raman bands are. Theoretical and measured cross sections can be found in (McCreery, 2005), some of which are listed below in Table 3.3 and used in this model.

Sample	Raman band (cm ⁻¹)	Cross section (cm ² /sr mol x10 ³⁰)
Cyclohexane	802	5.2
O ₂	1555	0.58
SO ₄ ²⁻	981	9.9
H ₂ O	1595	0.11
β-carotene*	1520	1.1x10 ⁷
Glucose	1126	5.6
Carbon (diamond)	1332	3.4

Table 3.3: A table of Raman cross sections for specific scattering bands for various materials. Taken from (McCreery, 2005). All cross sections were measured with the materials in gaseous or aqueous form. *β-carotene cross section was not measured directly but using measured using a benzene band comparison, using a 514nm excitation wavelength.

MODELLING SAMPLE RESPONSE

Using the laser intensity and several properties of the sample it is possible to calculate the intensity (Watts m⁻²) of the Raman scattered light I_R ,

$$I_R = I_0 \sigma_j N dz \quad 3.11$$

where I_0 is the laser irradiance at the sample (in Watts m⁻²), σ is the integrated cross section of a Raman band j (with the units cm⁶ molecule⁻¹), N is the number density of the sample (in cm⁻²) and dz is the path length of the laser in cm.

If the sample is particularly absorbing the absorption length can be used (given by Equation 3.12),

$$dz = (\alpha_L + \alpha_S)^{-1} \quad 3.12$$

where α_L and α_S are the absorption coefficients for the laser and scattered light respectively. The coefficients are calculated using Equation 3.13

$$\alpha = \frac{4\pi k}{\lambda} \quad 3.13$$

where λ is the wavelength of the absorbed light and k is the extinction coefficient of the material. Extinction coefficients can be found in the literature of material properties. Often the smallest value of each of these definitions is used to calculate a minimum scattering intensity.

It may be necessary to calculate the number of photons per unit second being emitted from the sample. A theoretical photon rate can be derived using Equation 3.11 in conjunction with Equations 3.14 and 3.15,

$$I_R = P_R hc (\bar{\nu}_0 - \bar{\nu}_j) \quad 3.14$$

$$I_0 = P_0 hc \bar{\nu}_0 \quad 3.15$$

where P_r and P_0 are the photon rate (photons s⁻¹ m⁻²) of the Raman scattered light and laser respectively, h is Plank's constant and c is the speed of light. The parameters ν_0 and ν_j are the frequencies of the laser light and Raman scattered light (for a particular mode). The result is given by Equation 3.16,

$$P_R = P_0 \sigma_j \bar{\nu}_0 (\bar{\nu}_0 - \bar{\nu}_j)^{-1} N dz \quad 3.16$$

Equation 3.16 is used by the model to calculate the photon scattering rate of a particular sample (photons s⁻² cm⁻²). As previously discussed however, σ is dependent on many factors so often the frequency independent counterpart to the cross section, σ_j^0 , is given. This can be converted to the frequency dependent cross section via Equation 3.16,

$$\sigma_j^0 = \frac{\sigma_j}{(\bar{\nu}_0 - \bar{\nu}_j)^4} \quad 3.17$$

Equation 3.16 clearly shows the ν^{-4} relationship with Raman intensities described in Chapter 1. Substituting this into equation 3.16 gives,

$$P_R = P_0 \sigma_j^0 \bar{\nu}_0 (\bar{\nu}_0 - \bar{\nu}_j)^3 N dz \quad 3.18$$

Often Raman cross sections are frequency dependent and are stated with their corresponding band position. The Raman scattering cross sections listed in Table 3.3 were used in conjunction with Equation 3.18 to calculate the scattering intensity of a specific vibrational mode.

This subsection of the radiometric model derived the sample radiant exitance (scattering intensity). This is the intensity of the scattered Raman light either in units of W cm⁻² or photons s⁻¹ cm⁻² (using Equations 3.17 and 3.13 respectively).

3.2.4 INPUT OPTICS AND COUPLING

This part of the radiometric model describes the performance of the system collection optics and the coupling to the spectrograph. The model uses parameters from previous sections such as the radiant exitance of the sample and the focused laser spot diameter (the diffraction limit of the laser) to calculate the radiance of the sample. The radiance is defined as the radiant flux emitted by a surface per unit solid angle per unit area of the sample. The Raman scatter from the sample emits radially and therefore the number of photons in a given subtended area will decay according to a square root law.

Using the telescope configuration and the known geometry of the system, the model describes the collection power of the system based on the collection solid angle. The collection solid angle is the angle subtended by the telescope (with a certain aperture size) relative to the sample surface. The collection solid angle is highly dependent on the height of the sample (relative to the instrument) and the working distance. The model also accounts for the losses due to the obstruction of the secondary mirror, imperfect lens transmission (see Sections 3.1.3 and 3.2.2) and optical fibre coupling.

MODELLING SYSTEM INPUT OPTICS

In order to determine the power collected by the telescope (i.e. the number of photons per second) the model first uses the radiant exitance, I , from Section 3.2.2 to calculate the radiance, L_0 . In the first instance the radiance, L_0 , normal to the sample surface is calculated using Equation 3.19,

$$\frac{dI}{d\Omega} = L_0 \quad 3.19$$

where Ω is the solid angle. Since the sample emits the scattered light radially, the solid angle is assumed to be 4π . Since it is possible that the telescope is not located at 90° to the sample surface, it is important to calculate the radiance at the angle θ , L_θ ,

$$L_\theta = L_0 \cos(\theta) \quad 3.20$$

Finally, the sample with excited area dA is referred to as an extended source (rather than a point source). The radiant intensity, I_e (defined as the power emitted from a surface sr^{-1}), is calculated using Equation 3.21,

$$I_e = L_\theta dA \quad 3.21$$

To find the power intercepted by the telescope aperture, the solid angle subtended by the primary, $d\Omega_T$, is calculated. This is given by Equation 3.22:

$$d\Omega_T = A_T D^2 \quad 3.22$$

where A_T is the area of primary mirror and D is the distance to the sample. The total power collected by the telescope, P_T , is calculated by multiplying the radiant intensity of the sample by the solid angle subtended by the telescope,

$$P_T = I_e d\Omega_T \quad 3.23$$

The light collected by the telescope initially passes through the correcting lens, which has a transmission efficiency of ~93% in the 532nm-700nm wavelength range. Secondly, due to the configuration of the Cassegrain-Mustov telescope design, the secondary mirror obstructs a fraction of the incoming light. The percentage of incident light that is obstructed is calculated using Equation 3.24,

$$\left(\frac{D_{secondary}}{D_{primary}} \right)^2 \times 100 = \text{obstruction \%} \quad 3.24$$

where $D_{secondary}$ and $D_{primary}$ are the diameters of the primary and secondary mirrors respectively. In addition, the mirrors will have a reflection coefficient that quantifies the amount of light that is successfully reflected and not scattered or absorbed. The secondary mirror then focuses the light into a lens, L3, held in a lens tube at the back of the telescope (see Figure 3.9 for diagram and description of the set up). Accounting for the mirror and lens efficiencies, Equation 3.25 describes the amount of light entering the optical probe (located at the back of the lens tube),

$$P_{OP} = \left(\frac{D_{secondary}}{D_{primary}} \right)^2 T_{correcting} T_{primary} T_{secondary} T_{L3} \quad 3.25$$

Light entering the optical head is collimated by a lens (i.e. L4 in Figure 3.9) and is subsequently filtered by a notch filter. The notch filter transmitted light of a wavelength of 532nm (with a fixed efficiency) and reflects (into a separate optical path) light at longer wavelengths, such as the Raman scatter from mode j (see Section 3.2.2). The optical power (or T) is given by Equation 3.26:

$$P_{notch,j} = P_{OP} T_{notch} \quad 3.26$$

After the collected light has been filtered, it is focused onto the end of an optical fibre by lens, L5. The optical fibre will then internally reflect the light along the fibre to the spectrograph. Again, L5 will have a transmission efficiency that describes the fraction of the incident light that is transmitted. The total loss in signal through an optical fibre is the summation of the fibre attenuation km^{-1} , connector losses and splice losses (see Section 2.1.4 for specific details). Equation 3.26 uses the power loss through L5 and the total fibre loss, F_{loss} in dB, to give the optical power arising from the sample that reaches the spectrograph,

$$P_{spectrograph} = 10 T_{L5} P_1 \left(\frac{F_{loss}(\text{in dB})}{10} \right) \quad 3.27$$

$P_{spectrograph}$ is the total optical power reaching the spectrograph from a given Raman vibrational mode j . This can be converted to the number of photons per second, n , using Equation 3.28:

$$n = \frac{P_{spectrograph} \lambda}{hc} \quad 3.28$$

where λ is the wavelength of the photons, h is Planks constant and c is the speed of light. This section has not described the losses due to misaligned lenses (as this has been described in Section 3.2.2). However the losses still have to be accounted for.

The output of this section of the radiometric model is the power (or number of photons) transmitted through the collection optics.

3.2.5 SPECTROGRAPH

This section describes the behaviour of light as it progresses through the spectrograph based on its intensity and wavelength. The collected light will enter the spectrograph through the aperture of the fibre optic. The light is then collimated by a lens or set of lenses. The model uses the lens diameter and focal length to describe the collection power of the lens (see Figure 3.23) and the transmission efficiency to calculate the throughput of the lens.

The light interacts with a diffraction grating before being focused onto the detector plane. The model describes the grating and its effect on the incoming light based on slit parameters, such as the density (the number of slits or grooves per meter on the surface of the grating), width and separation (labelled in Figure 3.25). The grating will diffract light away from the plane of the incident beam (see Figure 3.25). This section of the model will calculate the intensity of light at a given wavelength (the wavelength of a specific Raman band) at the detector plane within a given diffraction order.

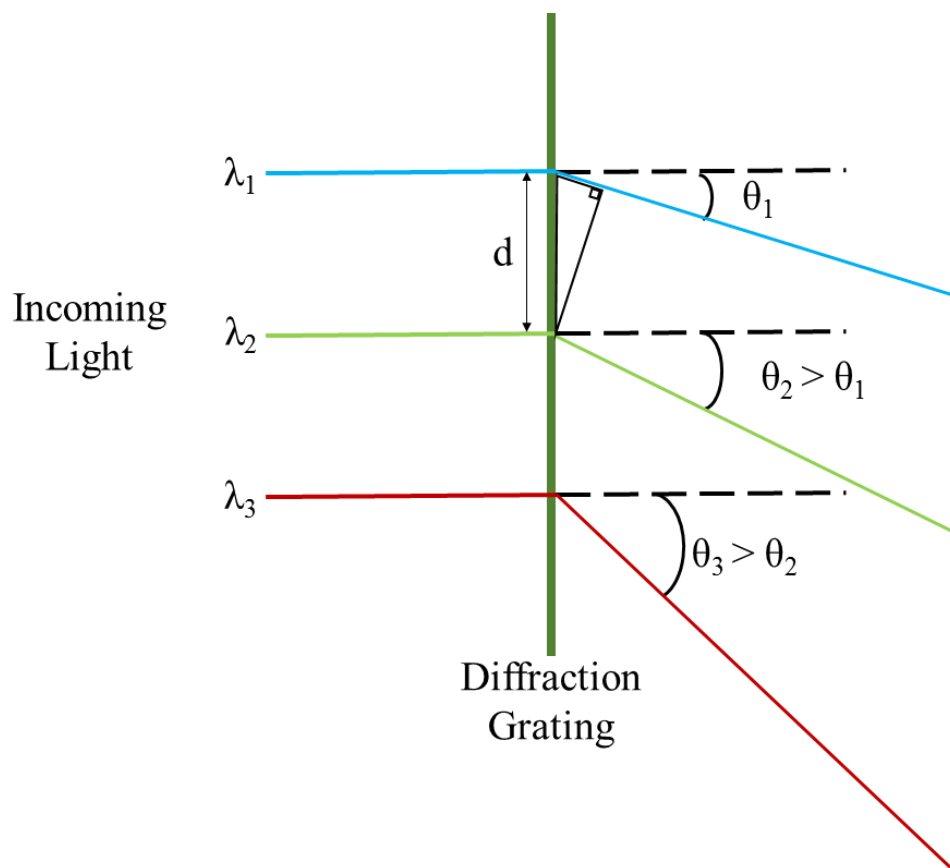


Figure 3.25: A diagram illustrating the dimensions and diffraction grating and the diffraction geometry of incident light.

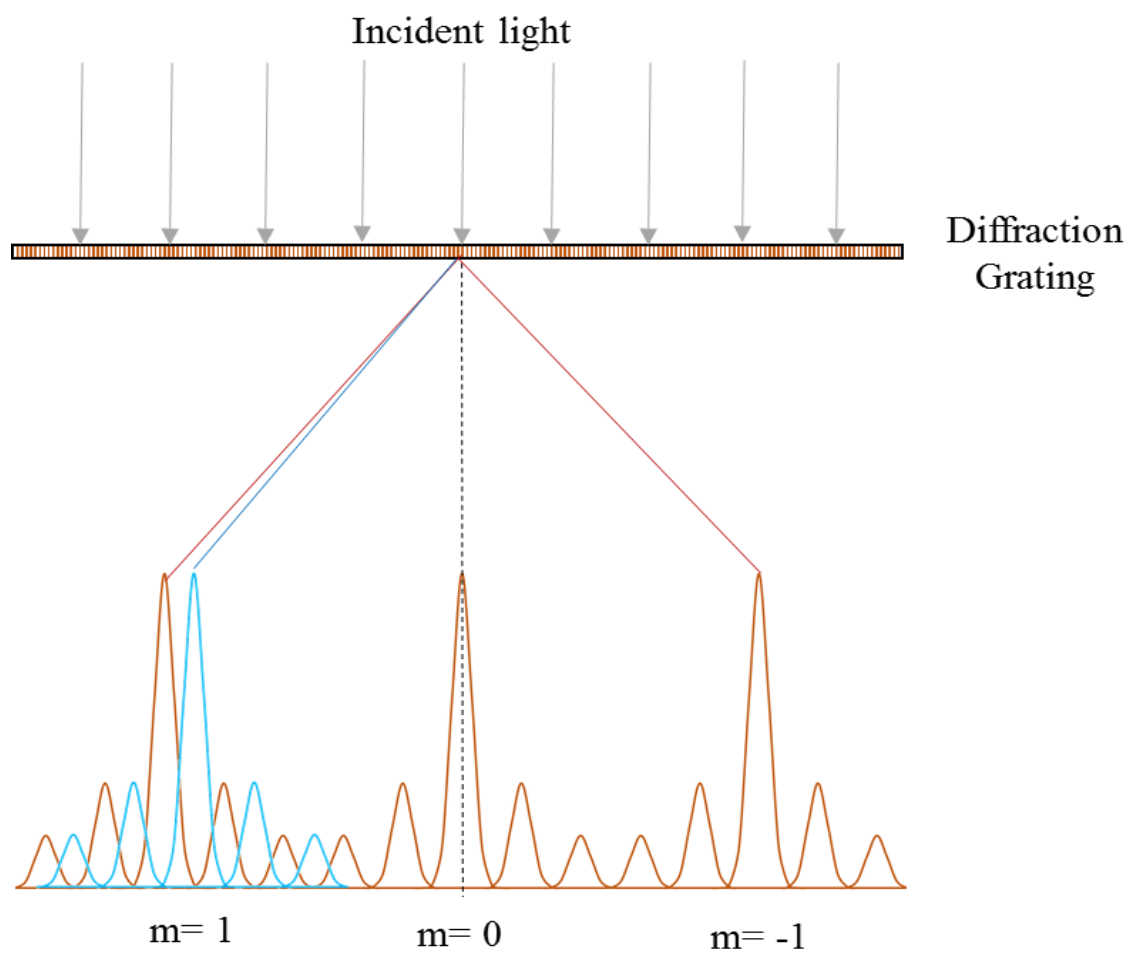


Figure 3.26: A diagram to show the intensity of diffracted light with respect to the diffraction order.

MODELLING SPECTROMETER PROCESSES

Light enters through an optical fibre into the spectrograph. The fibre optic acts as the slit to the spectrometer, the numerical aperture of which influences the angle at which light enters. If the slit aperture and the lens are misaligned, photons will be lost from the system (see Section 3.2.2 for a discussion about numerical aperture matching). The light from the optical fibre is then collimated using a lens (or set of lenses) which is NA matched to the fibre aperture. The collimating lens has a transmission efficiency of 95%, resulting in 5% of light being absorbed and reflected by the lens. The resultant intensity, $I_{grating}$, is calculated using Equation 3.29:

$$I_{grating} = I_{spectrometer} T_{L6} \quad 3.29$$

where $I_{spectrometer}$ is the power of the incident light onto the lens (from the optical fibre) and T_{L6} is the transmission efficiency of the lens, L₆. The collimated light is then incident on a diffraction grating, which has a specific transmission efficiency. Photons are then diffracted at a small angle, θ , (proportional to their wavelength and the parameters of the diffraction grating) into a diffraction order

The sine of the diffraction angle is given by Equation 3.30:

$$\sin \theta = \frac{m\lambda}{d} \quad 3.30$$

where m is the diffraction order index ($\pm 1, \pm 2$), λ is the wavelength of incident light and d is the separation distance between slits in the grating. The intensity of the light at that position in the diffraction order is given by Fraunhofer's equation for a diffraction pattern with N slits;

$$I_{\theta} = I_0 \cdot \left(\frac{\sin \beta}{\beta} \right)^2 \cdot \left(\frac{\sin N\gamma^2}{\sin \gamma^2} \right) \quad 3.31$$

where I_0 is the intensity of the wavelength at $\theta = 0$ ($m=0$ order), N is the number of slits illuminated by the collimated beam and β and γ are given by,

$$\beta = \frac{\pi a \sin \theta}{\lambda} \quad 3.32$$

and

$$\gamma = \frac{\pi d \sin \theta}{\lambda} \quad 3.33$$

Equation 3.31 describes the intensity of diffracted light compared to that in the 0th order ($m=0$). Since an absolute intensity at this position requires a quantum mechanical analysis of the incident wave-front, this model assumes that there are only 5 diffraction order generated by the grating, $m=0$, ± 1 and ± 2 . In reality there could be an infinite number of orders but each will be a very small fraction of the intensity of the previous order. By assuming that a negligible amount of incident light was diffracted into higher orders compared to the first 5 orders, the model can estimate how much light has been redirected into a specific order. Equation 3.34 give the intensity of a specific wavelength at $\theta = 0$ ($m=0$ order),

$$I_0 = \frac{I_{grating} T_{grating}}{1.1026} \quad 3.34$$

where $T_{grating}$ is the transmission efficiency of the grating. Equations 3.32, 3.33 and 3.34 are used to find I_θ .

Next, the model simulates the spatial redistribution of a particular Raman band of wavelength λ . Light exiting the grating exhibits a Gaussian profile within the diffraction order, see Figure 3.26. The model simulates this effect by firstly assuming an unconvolved diffracted band would have a diameter equivalent to the beam incident on the grating. The model then convolves the diffracted beam with a Gaussian function as described by Equation 3.35:

$$G(x, y) = \frac{1}{2\pi\sigma^2} e^{-\frac{(x-x_0)^2 + (y-y_0)^2}{2\sigma^2}} \quad 3.35$$

In practice, this is achieved using a grid that represents the grating output at the detector plane. The grid exhibits the same number of elements as pixels in the system's detector (for example, the grid would incorporate 1024 by 1024 elements if the detector was a CCD47-20). The values within the grid represent the number of photons per second at that particular location. Clearly most elements in the grid will be unpopulated but some elements (at locations given by Equation 3.30), will contain values representing the number of diffracted photons of a particular wavelength per second, I_θ . Figure 3.26 shows how the detector plane is described using a discrete array of elements.

The Gaussian kernel is variable in size and width depending on the level of redistribution needed. The grating output grid is firstly normalised (depending on the size of the kernel used) and then convolved with the Gaussian profile. As a result, features within the resulting matrix (including the diffracted band) are broader and less intense than those in the original grid.

Before the resulting matrix can be used to represent the light incident on the detector, the model simulates two more effects: the intensity loss due to transmission through the detector lens, L7, and the effects of optical convolution by all of the lenses in the system. The intensity of the light after transmission through the L7 is given by:

$$I_{detector} = I_0 T_{L7} \quad 3.36$$

where T_{L7} is the transmission efficiency of L7. The resulting grid is then convolved using a top hat (smoothing) function to simulate the effects of optical distortion by the lenses within the spectrometer. Like the Gaussian mask, the top hat kernel can be varied in size to alter the level of smoothing applied to the matrix. Once convolved, the resulting matrix represents the flux of light incident on the detector that arises from the spectrometer.

This section of the model outputs a Flux Grid that describes the distribution and intensity of Raman light reaching the detector plane. The array represents the total light exiting the spectrometer and accounts for attenuation and redistribution by both the grating and input/output optics.

3.2.6 DETECTOR

The Flux Grid described in the previous section includes intensity and spatial information relating to the Raman spectral signal generated by the sample, in photons per second. Each element of the grid represents a detector pixel and the value within the element denotes the number of Raman photons incident on that pixel.

This section of the radiometric model firstly determines appropriate signal background levels for the Flux Grid, such as ambient light and fluorescence emission from the sample. This background signal is then added to the grid elements containing the diffraction order. The wavelengths and intensity of the emitted fluorescence vary strongly from sample to sample and therefore the levels used in the model were determined during experimental

tests (see Chapter 4). The ambient light levels depend on the environment in which the system is operating and therefore have also been estimated following a number of experimental tests (see Chapter 4). The ambient light levels (which may not be uniform across the grid) are added as two separate components to simulate the ambient light at the detector and the ambient light collected by the input optics.

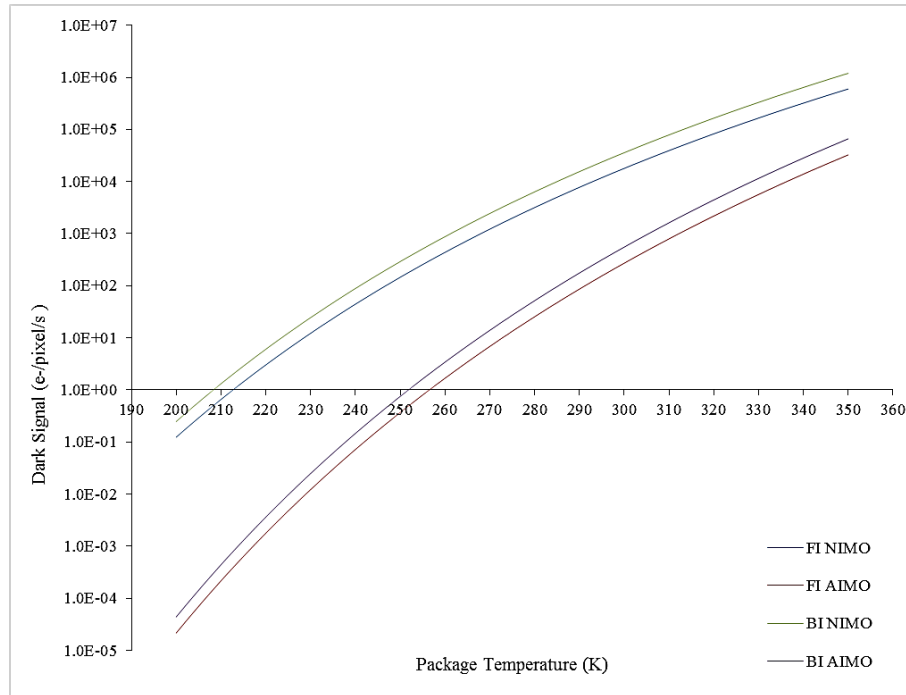


Figure 3.27: A plot to show how dark current varies with package temperature. Curves are shown for front illuminated, back illuminated and devices operating in advanced inverted mode and non-inverted mode.

Using the Flux Grid, the model subsequently calculates how a particular detector will respond and measure the incoming photons to produce a digitised image. To do this the model uses detector parameters such as the quantum efficiency (the efficiency with which incident photons produce electrons within the silicon substrate of the detector), the full well capacity and the responsivity. The full well capacity (FWC) is defined as the number of electrons that each pixel is able to hold before blooming occurs. The responsivity is the voltage that is produced at the output of the device per electron. For a CCD47-20 the FWC and responsivity are 100,000 e^- and 4.5 $\mu V/e^-$ respectively (e2v technologies, 2007).

The model also estimates an overall noise level, based on the incident signals and the detector operating mode (for example on-chip pixel binning). The dark noise is calculated using the system integration time along with a detector specific dark current rate. The dark current rate depends not only on the operating temperature of the device, but also

the detector architecture/operating mode (e.g. non-inverted mode operation, advanced inverted mode operation or the use of dither mode clocking). The parameters that dictate the dark current rate (based on detector properties) are given in the data sheets supplied by e2v technologies (2007). Like the electrons generated by incident photons, the dark current exhibits statistical fluctuations known as dark noise. The dark noise is defined as the square root of the dark current (i.e. the shot noise of the signal) and is dependent on the operating temperature of the device (as shown in Figure 3.27). The model also accounts for read noise. Read noise is a result of uncertainty in the sampling process of the CCD output and increases with readout speed. For readout frequencies of 500KHz a typical read noise value is between 5 and 15 electrons. A full discussion of read noise is given in Chapter 2, section 2.2.1.

This part of the model then produces a digitised value (based on the digitisation resolution which may be for example, 14 bits) and a signal-to-noise ratio for every pixel (or group of pixels) that is sampled by the electronics. Note that Chapter 5 describes how a Monte Carlo simulation can be used to model detector operation in more detail, accounting for statistical variations in the system output.

MODELLING SYSTEM DETECTOR PROCESSES

Initially, a level of fluorescence emission and ambient signal are added to the detector flux grid that was created in Section 3.2.5. The fluorescence signal, $I_{fluorescence}$ is only added to the elements/pixels that will contain charge generated by the diffraction order. An ambient light level, $I_{ambient}$, is added to every element in the flux grid but not equally as the distribution of ambient light may be non-uniform. As a result of this, an element within the flux grid describes the total number of photons incident on an individual detector pixel each second (see Figure 3.28).

Next, the photon flux is converted to a specific number of electrons, N_e , for each pixel using Equation 3.37:

$$N_{e-flux} = (I_{\theta} + I_{fluorescence} + I_{ambient}) t_{int} QE \quad 3.37$$

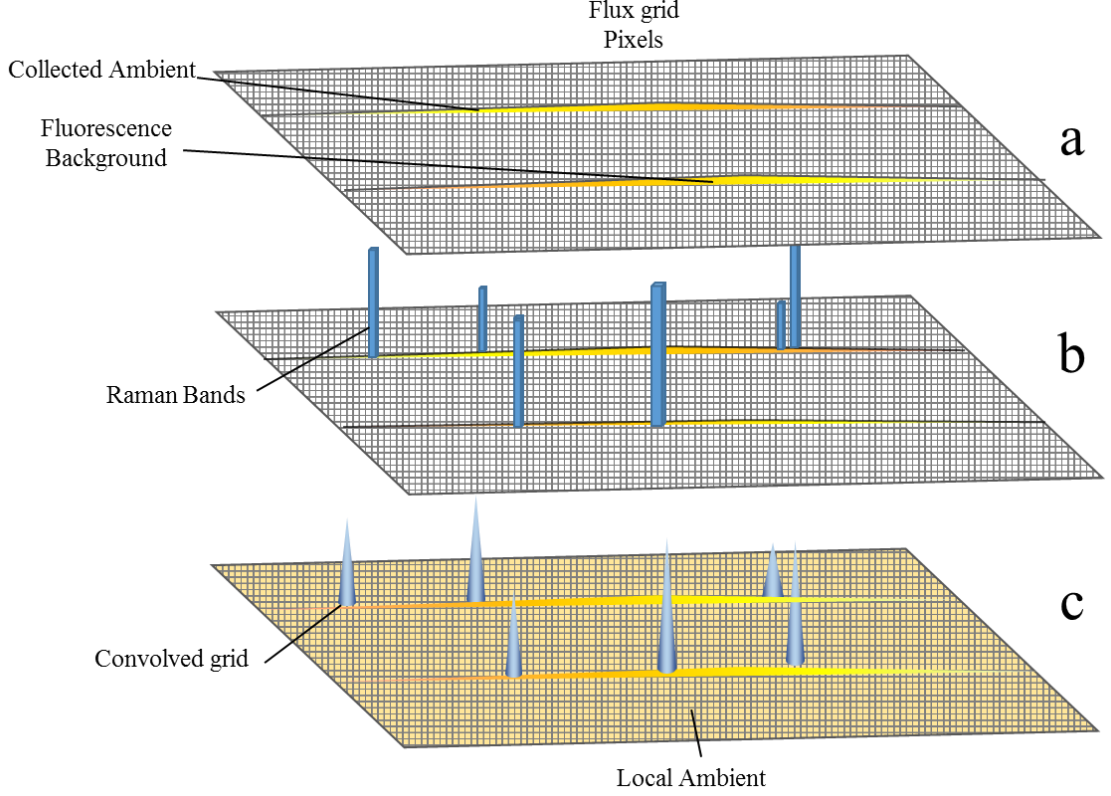


Figure 3.28: An illustration of the flux grid created by the model to represent the incident light on the detector. The structures are not to scale.

where, t_{int} is the integration time, and QE is the quantum efficiency of the detector. This is repeated for all elements within the matrix. Now, the grid describes the charge level within each pixel that results from the input signal and is referred to as the charge grid.

The signal in each pixel has an associated statistical poissonian noise, δ , given by

$$\delta_{e-flux} = \sqrt{N_{e-flux}} = \sqrt{\delta_{Raman}^2 + \delta_{fluorescence}^2 + \delta_{ambient}^2} \quad 3.38$$

The total noise from the various signal sources can be found by adding the individual noise levels (in electrons) for each signal in quadrature.

During the integration time, additional electrons enter the pixel as a result of thermal excitation within the silicon lattice (dark current). A more detailed description of dark current can be found in Section 2.2.1. The dark current rate, I_{dark} , for each pixel is calculated using Equation 3.39.

$$I_{dark} = I_{d0} X T^3 e^{-\frac{Y}{T}} \quad 3.39$$

where I_{do} is the dark current at a temperature of 293K, T is the detector operating temperature and X and Y are constants that are dependent on the detector format and material. For example, X and Y become 1.14×10^6 and 9080 respectively when calculating the dark current rate for a CCD47-20. The total number of electrons in each pixel due to dark current, N_{e-dark} , after the integration time, t_{int} , is given by Equation 3.40.

$$N_{e-dark} = I_{dark} t_{int} \quad 3.40$$

Poissonian noise associated with the dark current (often referred to as dark noise) is given by,

$$\delta_{dark} = \sqrt{N_{dark}} \quad 3.41$$

After t_{int} seconds, the total number of electrons in each pixel, $N_{e-pixel}$ is equal to,

$$N_{e-pixel} = N_{e-dark} + N_{e-flux} \quad 3.42$$

where $N_{e-pixel}$ is less than the FWC of a pixel. If the total number of electrons in each pixel is more than the FWC, the detector reaches saturation. The noise on the level of charge in a pixel is given by the equation

$$\delta_{pixel} = \sqrt{\delta_{e-dark}^2 + \delta_{e-flux}^2} \quad 3.43$$

After the integration period, the charge packets are shifted down into the serial register. If on-chip vertical binning has been implemented, then both the signal and the noise are increased. The signal is multiplied by the number of vertical bins, n_{bins} ,

$$N_e = N_e n_{bins} \quad 3.44$$

The charge is then shifted through the serial register onto the output node of the CCD. At this stage, horizontal binning can be modelled by using Equation 3.44 where n_{bins} is the desired number of horizontal binned pixels.

The charge packet in each pixel is then converted to a voltage using the output node (capacitor) of the CCD. The output voltage of the CCD is then amplified, sampled and digitised by the proximity electronics. A more detailed description of the readout process is given in Chapter 2. During this process an additional source of noise, the read noise, is

added to the signal. This section of the radiometric model uses a fixed read noise from experimental measurements. The total noise, δ_{total} , in electrons is given by

$$\delta_{total} = \sqrt{\delta_{pixel}^2 + \delta_{read}^2} \quad 3.45$$

where δ_{read} is the read noise. Using the total signal and noise in each pixel, a signal-to-noise ratio can be calculated. Equation 3.46 converts the total signal within a pixel and associated noise into digital units.

$$e^- \text{ per ADU} = \frac{FWC}{ADU_{max}} \quad 3.46$$

where FWC is the full well capacity of a pixel and ADU_{max} is the maximum number of digitised units, i.e. the digitisation range. The signal in each pixel is then converted to Analogue to Digital Conversion Units (ADU) to produce a digital image of the light incident on the detector plane. Equation 3.45 describes the relationship between the total noise level, in electrons. The signal-to-noise ratio is given by Equation 3.47:

$$SNR = \frac{N_{ADU}}{\delta_{total \text{ ADU}}} \quad 3.47$$

where N_{ADU} is the signal in ADU and $\delta_{total \text{ ADU}}$ is the total noise in ADU.

The final section of the radiometric model uses the flux grid, which describes the incident light on the detector, to generate a digitised pixel value. The model then uses this pixel value and the calculated noise level to obtain a signal-to-noise ratio which quantifies instrument performance.

4 SYSTEM SIMULATION

Chapter 3 described the development of a radiometric model for Raman spectrometer instruments (including in situ and stand-off configurations). The model described each subsystem within the instrument: the laser, optical head, input optics, output optics and grating and also provided a top level description of the camera system. However, to fully optimise the performance of a Raman instrument, it is important to understand the many interrelated parameters and complex trade-offs involved in the design and operation of the overall camera system. The instrument simulator provides a method of exploring the effects of low level detector operations (such as specific clocking speed, pre-scan clocking, post scan clocking, windowing and dither mode clocking) and the effects of radiation damage. The overall impact of these detector modes and properties depend on many parameters (such as the number of pixels and their size, integration time, device architecture and radiation dose) and are heavily influenced by the various sources of noise in the system (as discussed in Chapter 2). For this reason, the simulator adopts a Monte Carlo model approach and operates at the individual pixel level. Monte Carlo models are frequently used to simulate systems with many degrees of freedom that do not evolve (grow or change) in a rigid predefined way (such as the diffraction grating described in Chapter 3 interacts with incident light) but in a stochastic way, where the output depends on a set of random numbers generated within the simulation. A Monte Carlo model can account for statistical fluctuations of parameters (such as noise) that affect the overall result, and is particularly appropriate for understanding the effects of traps introduced by radiation damage.

In conjunction with the radiometric model described in Chapter 3, the simulation produces a virtual CCD image and ultimately (through the use of data extraction algorithms) a modelled Raman spectrum. As parameters within the simulation are varied, the CCD images and subsequent spectra illustrate the effect that they have had on the

data, the SNR achieved by the instrument and the overall science capabilities of the instrument.

This chapter describes the software simulation process, highlighting where and how parameters can be altered to investigate the performance of specific instrument configurations or detector operating modes. It also highlights the impact that reducing the spectral resolution of the instrument and implementing non-optimised data extraction algorithms have on the overall scientific performance. The simulated SNR values achieved for various instrument operating modes (such as the implementation of stacked images and operating temperature) and type of excitation source (the use of a pulsed or a continuous laser) are also reported.

4.1 DESCRIPTION OF SIMULATION

The simulation is fundamentally based on three virtual grids: a Flux Grid, a Charge Grid and a Sample Grid (see Figure 4.1). Generally, the Charge Grid and Sample Grid contain the same predefined number of elements corresponding to the number of pixels within a detector utilised by a system. However, if required, the Flux Grid can contain a larger number of elements for finer resolution or for extended input fields (such as a moving image of the sky or a planetary surface) and the Sample Grid can extend for multiple frame readouts. The type of detector (and therefore the size of the Charge and Sample Grids) can be modified, depending on which system configuration is to be investigated.

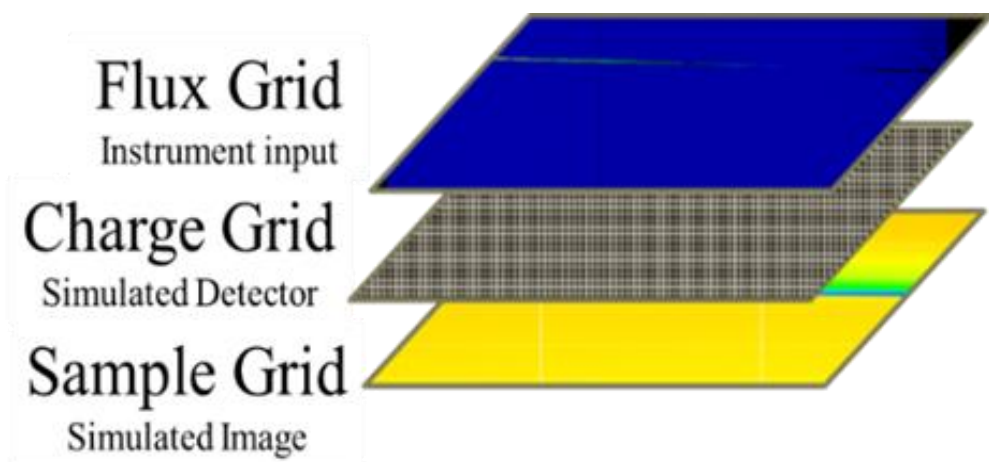


Figure 4.1: An overview of the data grids used within the software model.

Figure 4.2 shows the sequence of events that occur during the simulation with respect to the three virtual grids.

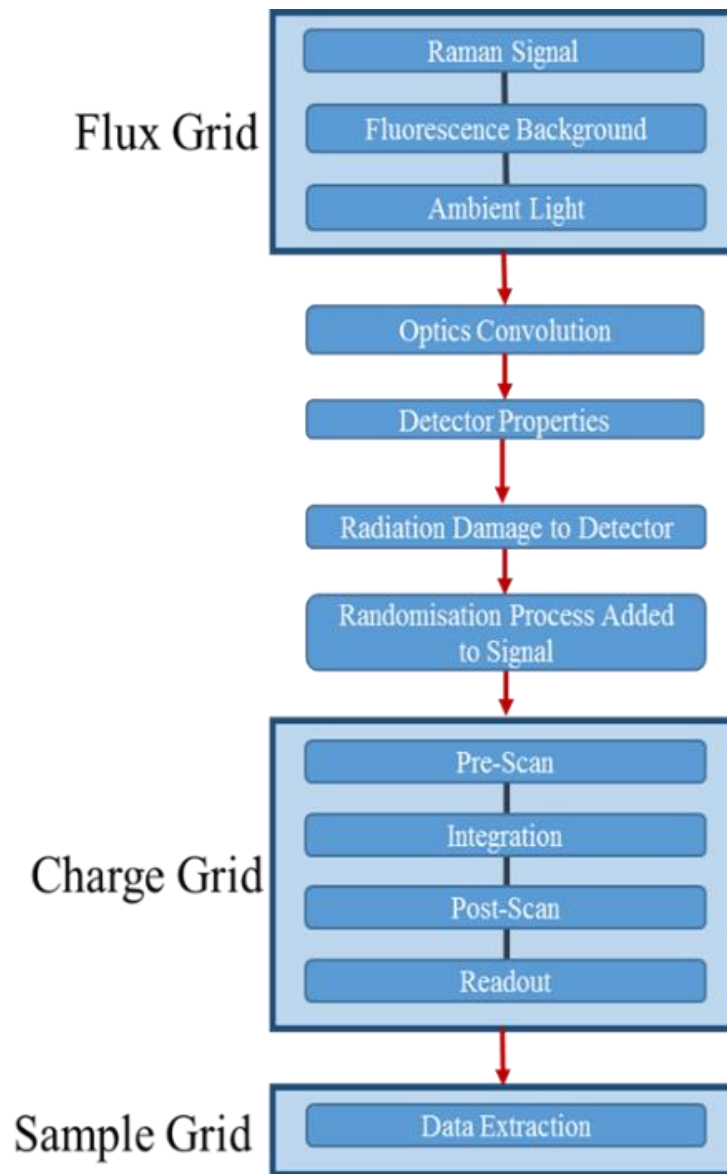


Figure 4.2: A flow chart that illustrates the sequence of processes that take place within the simulation.

4.1.1 FLUX GRID

Initially, the software calculates the signal that is expected to be generated by the spectrograph (i.e. the Flux Grid holds the spatially distributed version of this signal). The details of the processes involved in generating this input flux signal are described for the radiometric model in Section 3.3.6 of Chapter 3. This overlap between the simulation and

radiometric model (indicated by the dotted line in Figure 3.21) is essential to fully simulate the end-to-end instrument performance and to enable rapid investigations of complicated parameter trade-offs (in terms of their impact on overall scientific performance).

The Flux Grid contains both the Raman signal and fluorescence generated by the sample, as well as the ambient light from both the collection optics and that incident immediately onto the detector. The intensity and distribution of the background light depends on many factors, such as the sample, operating environment and the throughput of the system, all of which have been accounted for within the radiometric model (Chapter 3). The Flux Grid created in Section 3.2.6 of Chapter 3 gives the intensity and position of each Raman band in pixel coordinates (x-y plane of Figure 4.3) at the detector plane. The simulation adds fluorescence signal according to a model of intensity versus wavelength derived from spectral fits performed on a number of data sets acquired from planetary analogues

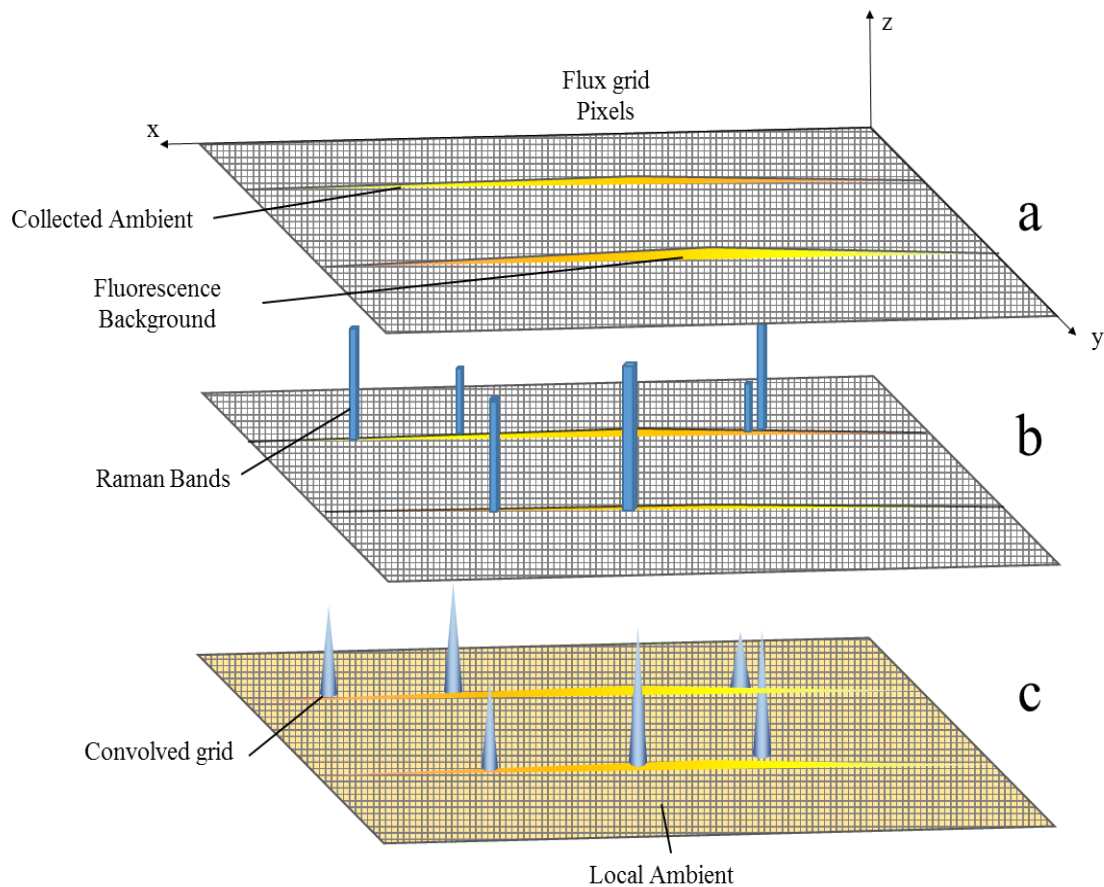


Figure 4.3: A diagram showing the dimensional layout of the flux grid. The diffraction order is created in the x-y plane while the intensity of the signal is displayed in the z direction.

in the laboratory (see Section 3.2.3 in Chapter 3) in order to create a pixel versus intensity profile in the x-z plane (see Figure 4.3).

The Raman bands are then superimposed onto the fluorescence profile produced by the radiometric model. In addition, an ambient light contribution, derived from experimental studies (see Figure 4.4), is also added to the profile.



Figure 4.4: A CCD image showing a varying level of ambient light incident on a detector.

At this point, the Flux Grid contains the ambient light that is collected by the instrument input optics along with the Raman signal and fluorescence. The signal profile is then spatially redistributed in the x-y plane (see Figure 4.3) according to the optical properties of the grating and the input/output lenses. The diffraction order curvature is modelled using polynomials (between 2nd and 7th order) and positioned appropriately on the surface of the detector, according to the specific configuration of the system. The curved signal profile is then convolved with an appropriate point spread function to simulate the effects of the system optics. The scale of the convolution order can be varied to account for a wide range of optical system responses. The signal is then dispersed across the detector plane in accordance with the specific properties of the grating, according to the diffraction process described in Chapter 3, Section 3.2.5. If appropriate, this process can be repeated to produce multiple diffraction orders within the Flux Grid. Finally, a secondary ambient light level is added to each element in the Flux Grid to represent the level of local (unaffected by the optics) ambient light that reaches the detector directly. An example of

a typical Flux Grid produced by a spectrometer with a single diffraction order is given in Figure 4.5.

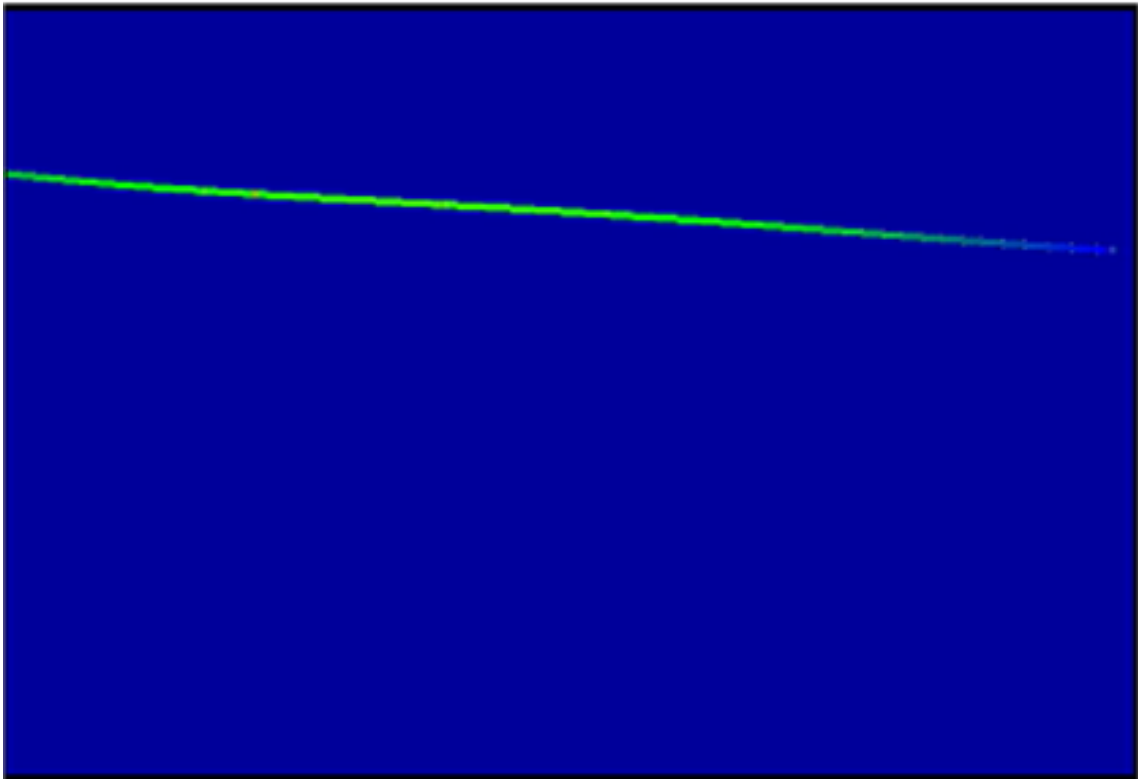


Figure 4.5: An example of a flux grid generated by the software.. The grid features a single diffraction order (containing the Raman and fluorescence signal) and a uniform ambient light background signal.

4.1.2 CHARGE GRID

The next stage in the instrument simulation is the generation of charge within the detector as a consequence of the incident light flux reaching the surface of the camera. The detector charge generation process is described in full in Chapter 2 (Section 2.2.1) and is modelled in Chapter 3, Section 3.3.6. The simulation software stores the charge level in each pixel in a Charge Grid. Initially, the Charge Grid is an empty array of elements, identical in size (format) to the detector within the modelled system (see Figure 4.1). Depending on the detector type, the software accounts for a number of different device properties (such as quantum efficiency, pixel size and full well capacity) when determining the charge generated in the Grid, all of which influence the level of charge that accumulates in each element (i.e. each pixel integrates the corresponding signal in the flux grid, accounting for QE, for the duration of the integration period unless the full

well capacity is reached). In parallel to this process, additional dark current charge is added to each pixel, according to the level that the detector type and specific operating temperature of the detector would produce. Figure 4.6 shows how the charge grid evolves throughout the integration period. The final signal in each pixel is randomly drawn from a Poissonian distribution, with the mean of the distribution set to the signal level produced by the integration process described above. This simulates the statistical variation expected when sampling the light intensity incident on the surface of the detector.

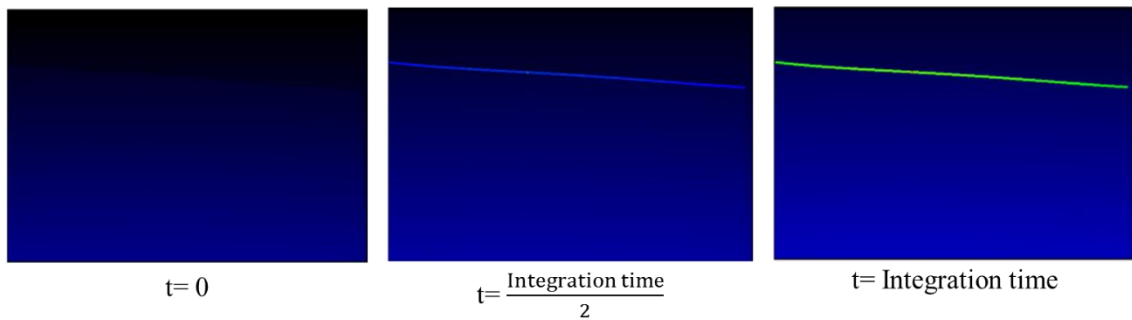


Figure 4.6: Screenshots from the simulation showing how the charge grid develops during integration time. The screen shots were obtained during the integration stage where values in the charge grid vary over a set period of time (the integration time) according to the corresponding levels in the flux grid. The three screen shots were obtained at the beginning of the integration process, at $t=0$ after the pre-scan had ended, mid-way through the process and at the end just before the simulated sampling.

4.1.3 READ OUT AND SAMPLE GRID

The radiometric model is capable of simulating many readout operations including the pre-scan process, windowing, dithering, post-scan (clocking out additional pixels that may not contain signal) and on-chip binning. To perform these operations in a flexible way, the software uses parameters to represent the number of rows and columns, the charge transfer times (serial clock frequency) and the properties of the serial register (e.g. charge capacity). Using these parameters in different combinations, the software is able to simulate a wide variety of readout processes. For example, to simulate clearing a 2048 by 2064 pixel device of charge, the software would simulate 2064 parallel row shifts (in order to move charge across all regions on the Charge Grid and into the serial register) without serial register clocking. A pre-scan operation is usually implemented if the detector is continuously exposed to signal from the sample or ambient light during the readout process (i.e. if a mechanical shutter is not included in the system). In this case,

there is a gradient in the charge level from the bottom to the top of the device, as illustrated in Figure 4.6, at $t=0$ (prior to the integration period). This results from the fact that when the full device is cleared, the top row begins to integrate dark signal (and signal if it is exposed to light) and the accumulated charge is then passed onto the row below (this process is repeated all the way down the device) such that the bottom row contains more charge than the top row by the time the integration period starts.

During simulation of the charge readout process (the shifting of pixel charge onto the output node for measurement and digitisation), the software creates a Sample Grid. This array contains all the data that has been read out from the CCD (i.e. pixel charge that has been shifted onto the output node and subsequently digitised). Compared to the Flux and Charge Grids, the size of the Sample Grid depends on the specific readout operations implemented by the simulation. For example, the Sample Grid can include additional pixels that are not connected to the light sensitive part of the CCD (i.e. where the serial register incorporates some extra pixels to aid noise characterisation) or additional virtual pixels that arise from continuing the readout process beyond the length of the serial register (i.e. overclocking).

It should be noted that the charge transfer/readout time can be reasonably significant for large devices and/or slow readout frequencies and in some cases it is necessary to implement windowed readout modes if the interesting signal is limited to specific regions on the surface of the detector. To simulate windowing operation, a fraction of the total number of rows (set at the start of the simulation) that do not include signal are shifted rapidly into the inactivated serial register (but are not clocked onto the output node). Once the charge generated by the signal has reached the serial register, the read out sequence is initiated and the row transfer time is increased to allow all of the data in the row to be sampled with an appropriate low level of noise. The rows located above the interesting regions, that also do not contain useful data, are subsequently shifted rapidly through the Charge Grid before the next frame is acquired.

For devices that incorporate a frame store, the Charge Grid is expanded vertically by the same number of rows as is present in the light sensitive area of the CCD. The simulated signal (residing in the top half of the grid) is then clocked rapidly through the image area into the rows in the bottom half of the device (where the pixels are subsequently read out at the user defined speed while the next frame is acquired).

After each action (such as the shift of a pixel row), the Charge and Sample Grids are updated to determine the level of signal in each pixel (for example, the build-up of dark current during read out) and the progression of the read out process. It is also during CCD readout operations that the effects of radiation damage become significant. As the Charge Grid is manipulated to simulate charge shift, the software uses (previously calculated) capture and release probabilities to determine if a given trap will change status (i.e. become filled or empty) as the simulated readout progresses (see Section 4.3). Image smearing or signal loss due to the traps can be seen on both the Charge and Sample Grids and the effects are also apparent in the extracted simulated spectra.

Figure 4.7 shows an example of an image produced by the software (Sample Grid) using the processes described in this chapter. The image contains a simulated spectrum of Beta-Carotene. The insert features the Raman bands (A) superimposed on the fluorescence emission (B), while (C) denotes the ambient light level. Labels (D) and (E) indicate the under-scan and over-scan regions of the simulated CCD detector output. The under-scan and over-scan regions are parts of the device created by performing the readout sequence without shifting charge from the device. In this process, read noise is added to digital data devoid of signal or dark current. The image also shows band trails (F) that arise as a consequence of device pre-scan and post-scan operations. This highlights a potential issue if a spectrometer produces several diffraction orders (i.e. below the order present in this image), as the trails from any one order result in contamination of the other subsequent orders.

The data are extracted from a region on the Sample Grid that is defined by a polynomial that encapsulates all of the signal associated with a particular spectral order. The data are binned appropriately (between the limits defined by the polynomials), to produce a plot of column intensity versus pixel position. If required, an SNR value can be calculated using either the extracted spectral data or the individual pixel values from the Sample Grid.

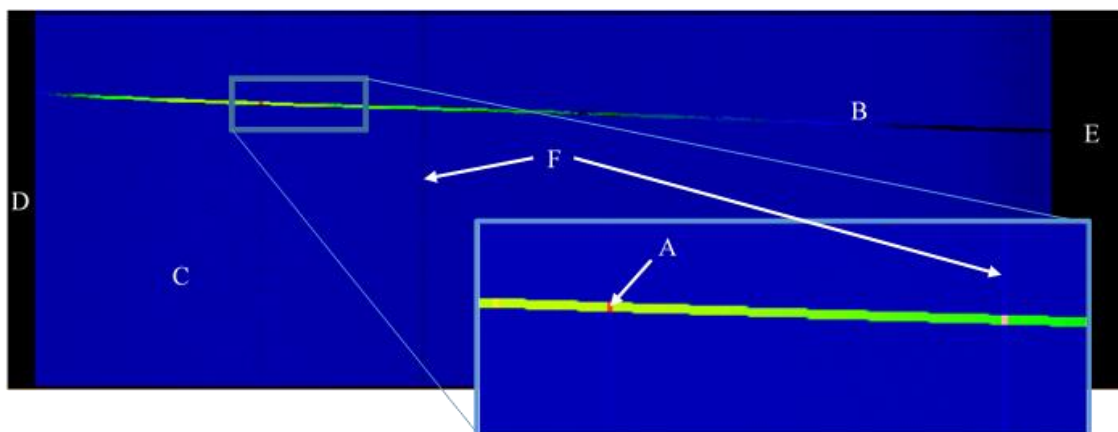


Figure 4.7: A simulated spectral CCD image of the organic compound, beta-carotene. The insert features a section of the simulated diffraction order where the Raman bands are particularly clear.

4.2 SYSTEM OPTIMISATION USING THE SIMULATION

4.2.1 OPERATING MODES: PULSED VS CONTINUOUS LASER

The simulation was used to compare the performance of an instrument that utilises a pulsed laser compared to one that utilises a continuous laser, under varying levels of ambient light. The model was based on standard pulsed and continuous lasers (the properties of which are given in Chapter 3, Section 3.2.2). The continuous laser was assumed to have a power of 80mW (which is similar to the levels adopted for the ExoMars Raman Laser Spectrometer (Moral *et al.*, 2016)).

Comparison between the instrument configurations is achieved by analysing the time required for each laser to deliver a fixed amount of energy to the sample. The fixed quantity of energy is the amount required to induce sufficient Raman emission from a sample and was chosen based on spectra obtained using the RLS proto-type (described in Chapter 1.3.4). The example spectrum, shown in Figure 4.8, suggests that 1 second of 80mJ of excitation energy from a continuous laser is sufficient to stimulate Raman emission in samples such as acetaminophenol. For a mineralogical sample such as quartz, 20 seconds of 80mJ (1.60J in total) is required to induce a sufficient Raman signal. In the simulation process the absolute signal levels (Raman and fluorescence emission) can be

scaled to represent those emitted by natural samples (i.e. the intensities measured differ due to additional factors such as crystallinity).

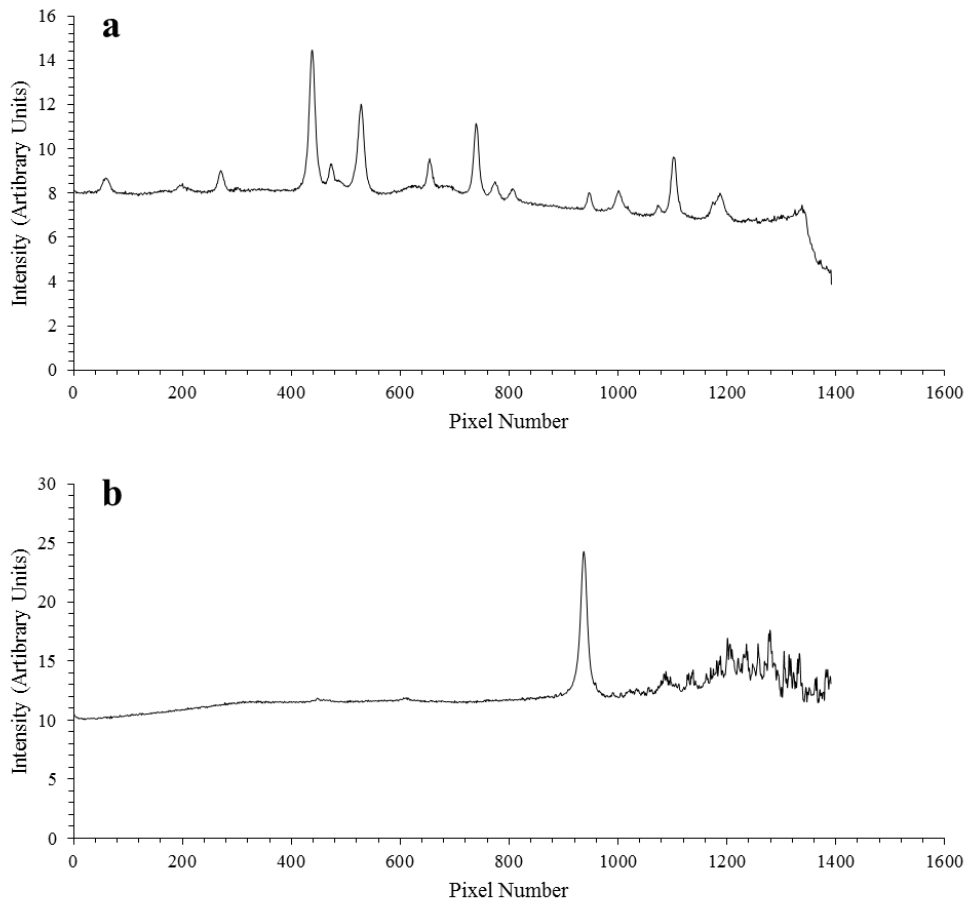


Figure 4.8: (a) A spectrum of paracetamol obtained using a 1 second integration time. Panel (b) shows a spectrum of quartz obtained using a 20 second integration. Both spectra were obtained using the RLS prototype.

The continuous laser (with power 80mW) can deliver 80mJ of energy to the sample in one second, but given the laser parameters listed in Table 3.2, the pulsed laser would deliver 80mJ to the sample in a total time of 0.23 seconds. This means that a detector operating with a continuous laser must integrate an incoming signal for 0.77 seconds longer than a detector working in conjunction with a pulsed laser, during which time it will integrate more ambient light and the level of dark current will have increased (compared to the level of the shorter integration time). This difference in integration time leads to a significant difference in the noise levels for the different configurations. The simulator uses the detector properties of a back illuminated CCD47-20 operated in advance inverted mode and the model assumes a detector QE of 60% at 532nm and a total

electronics read noise of $20e^-$. Using these values, an SNR is calculated to represent overall performance in that particular configuration.

This signal-to-noise calculation was completed several times while varying other system parameters such as the pulsed laser power, however the excitation source power is usually limited by the damage threshold of a particular sample. The detector operating temperature (and hence the level of dark noise) was also varied as it is important to understand the relative benefit of additional cooling (given the spacecraft budget issues associated with cooling systems and increased power consumption).

In order to determine the optimum excitation energy incident on the sample, simulations were performed to determine how the SNR varies with the level of ambient light collected for several different instrument configurations. Figure 4.9 shows this relationship for six different instrument configurations. Five of the configurations use a pulsed laser at varying laser powers (ranging from 0.05-0.5J, each delivered in 1 second). The figure also reports the SNR values achieved by an instrument using a continuous laser. Finally, Figure 4.9 shows the SNR variation observed (dotted line) for an instrument using a suggested maximum laser power of 100mW. This is the maximum amount of energy that should be delivered to a sample in order to avoid damage. It should be noted that this is

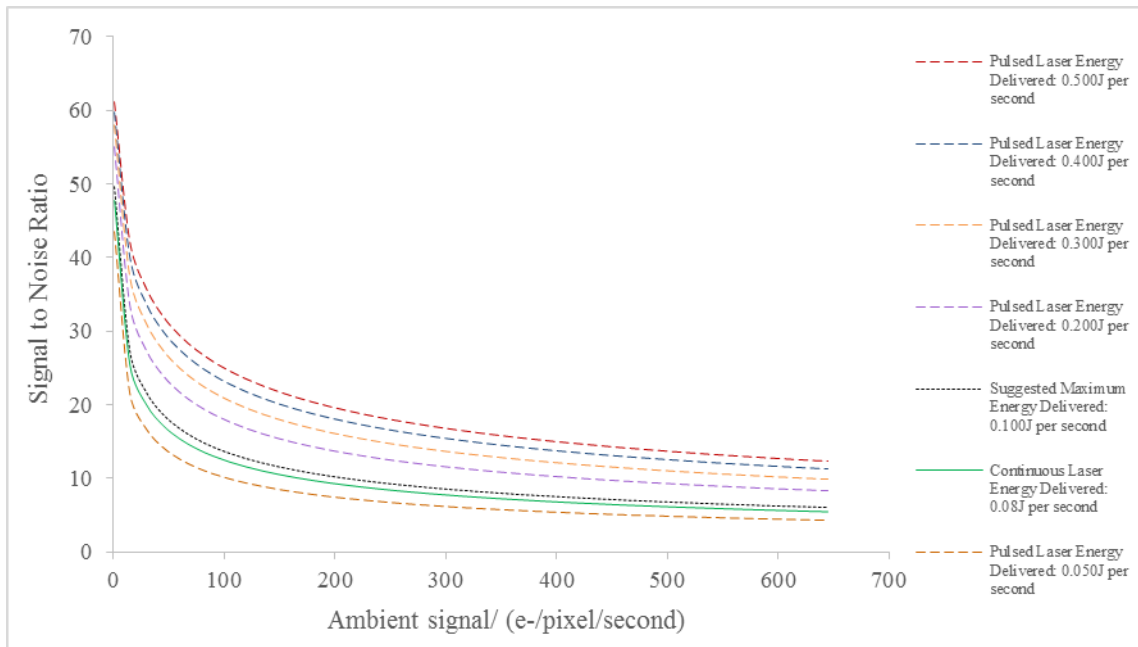


Figure 4.9: The theoretical relationship between the SNR achieved and the level of ambient light collected by the instrument. The plot shows the relationship for 5 different pulsed laser powers ranging from 0.05 to 0.5 J per pulse (dashed lines), as well as the SNR achieved when using a 80mW continuous laser (solid line) under various ambient light conditions.

not the laser damage threshold for all possible samples; studies in preparation for the ExoMars mission have suggested it should be used as an upper limit for the organic material that is hoped to be found on Mars (see, for example, Vandenabeele et al, 2012).

The results obtained from the simulator suggest that at low ambient light levels (<20 electrons per second) a continuous laser system can achieve an SNR of ~ 20 while the SNR values for the pulsed laser configurations range from 30 to 35 for incident energy levels in the range 0.2 to 0.4Js^{-1} . At high ambient light levels, such as 600e^- per second, the pulsed laser systems achieve SNR values ranging between 8 and 12 and the continuous laser system achieves an SNR of 4. Figure 4.9 also shows that the increase in the SNR gained by utilising a pulsed laser declines as the level of ambient light increases. However, it is clear that using a pulsed laser does provide a higher SNR compared to the continuous laser regardless of ambient light conditions.

Many of the energies used here are above the suggested maximum excitation energy meaning that the instrument configuration could damage the sample. The pulsed laser energy per pulse often used for stand-off Raman spectroscopy applications is 35mJ , which at a repetition rate of 10Hz delivers 0.35J per second to the sample. However, as described in Chapter 2, pulsed lasers often cause damage to materials by producing strong electric fields which can degrade a material by stripping electrons from the lattice structure (this is particularly problematic for dielectrics (Wood, 2003)). Pulsed lasers tend not to cause a significant amount of thermal damage compared to continuous lasers (Wood, 2003). As a consequence it is important to experimentally verify the damage thresholds for a pulsed laser instrument configuration in order to investigate a realistic upper and lower limit on the signal-to-noise ratio.

Another key aspect of the overall instrument performance is the effects of dark noise the impact of operating temperature of the detector. Figure 4.10 shows how the SNR achieved by two different instrument configurations (pulsed and continuous) vary with the level of ambient light collected by the instrument and the level of dark current produced by the detector. The SNR achieved for a given level of ambient light is shown for various detector operating temperatures ranging from -40°C to 40°C .

It is clear from the higher operating temperature curves ($>30^{\circ}\text{C}$) that the difference between the SNR achieved for pulsed and continuous lasers is negligible across all ambient light levels. This indicates that at this temperature high dark noise dominates over any decrease in ambient noise achieved using a pulsed laser. Both configurations achieve SNR values that are less than 3. As the detector temperature drops to 20°C , the SNR of both configurations is around 7 but deteriorates as the level of ambient light increases. The SNR achieved by a pulsed laser, however, does not decline as rapidly as the continuous laser; at 600 electrons/second of ambient light, the SNR of a pulsed laser system is 6.5 while the continuous system reaches an SNR of 4.5.

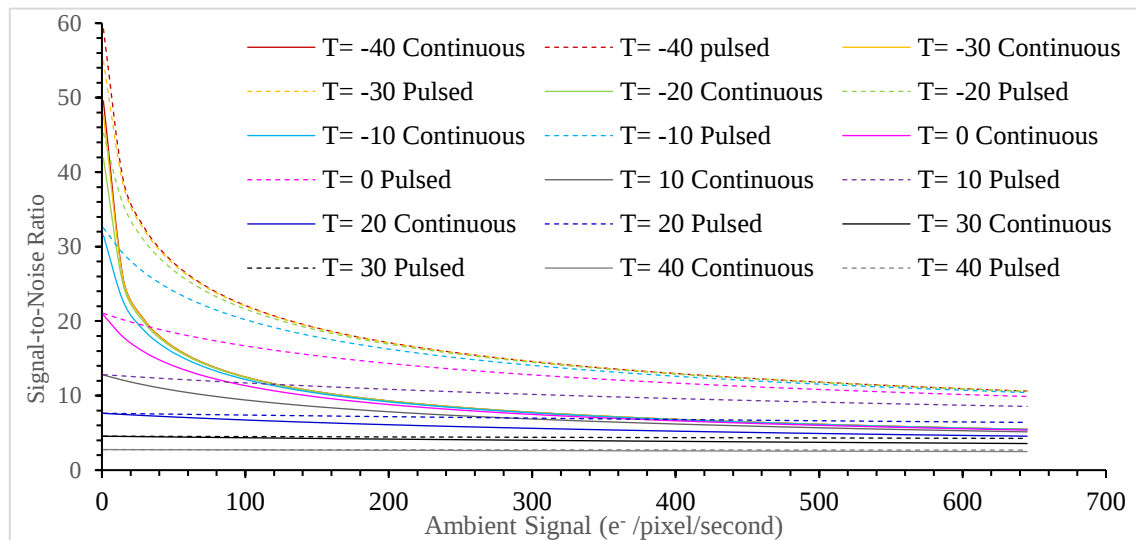


Figure 4.10: SNR achieved by two different instrument configurations varies as a function of the level of ambient light collected by the instrument. The plot also shows how the SNR relationship changes with detector operating temperature.

As the operating temperature drops further, the SNR of both configurations improves as the dark current within the detector is reduced. However, as the level of ambient light increases the SNR values in the continuous laser system rapidly decline in comparison to the pulsed laser systems.

The curves in Figure 4.10 also suggests that the SNR for the continuous system reaches an upper limit at a temperature of -10°C under higher levels of ambient light. For example, at ambient light levels of $<150 \text{ electrons s}^{-1}$, the SNR curves for operating temperatures of -10°C , -20°C and -30°C can be readily distinguished. However, the curves for detector temperatures of -30°C and -40°C are indistinguishable above $15 \text{ e}^{-}\text{pixel}^{-1}\text{s}^{-1}$. The curves for -10°C , -20°C , -30°C and -40°C become identical above an ambient light level of $150 \text{ e}^{-}\text{pixel}^{-1}\text{s}^{-1}$. This suggests that, depending on the environment conditions in which an instrument is operating (i.e. if the ambient light was $>150 \text{ e}^{-}\text{pixel}^{-1}\text{s}^{-1}$), cooling the detector beyond a certain temperature (such as -10°C) will have a negligible effect on the SNR achieved and would potentially waste valuable spacecraft resources (including operating time and power).

A similar trend is also apparent within the pulsed laser data produced by the simulator. The curves in Figure 4.10 that represent the SNR values achieved at -30°C and -40°C are indistinguishable at higher ambient light levels (i.e. $30 \text{ e}^{-}\text{pixel}^{-1}\text{s}^{-1}$) when compared to the equivalent continuous system curves. The -20°C curve reaches the SNR limit at levels around $200 \text{ e}^{-}\text{pixel}^{-1}\text{s}^{-1}$ (which is also higher than the corresponding continuous curves). This implies that cooling a detector will continue to increase the performance of a Raman system in higher levels of ambient light if the system utilises a pulsed laser.

4.2.2 OPTICAL REDISTRIBUTION

To simulate the effects of the system optics on the instrument input light, the Flux Grid is convolved with an optical point spread function. Figure 4.11 illustrates the effect of modifying the scale size (i.e. FWHM) of the function. The figure comprises 3 spectra extracted from images similar to those featured in Figure 4.8. In each case, the Flux Grid was integrated for a period of 2 seconds to generate the signal in the Charge Grid. Each image was then read out in an identical fashion, which included reading out the full device and implementing a pre-scan to replicate the dark current gradient observed in CCD images (see Section 4.1.2). Each plot was extracted from the corresponding image using the same [chi-squared fitted] polynomial at the same pixel position. The extraction process vertically co-adds the appropriate pixels within each step interval of the polynomial.

Plot A shows a spectrum convolved with an optics redistribution function with a scale size of 9 pixels while plots B and C show a system input (Flux Grid) convolved with scale sizes of 5 pixels and 3 pixels respectively. Clearly, the simulated Raman bands decrease in intensity as they broaden. As well as resulting in a decrease in SNR, the band shapes become less defined and their position may become more ambiguous, depending on noise levels. If this process is understood and modelled, images acquired using instruments that suffer from significant optical redistribution can be de-convolved and band positions more precisely determined.

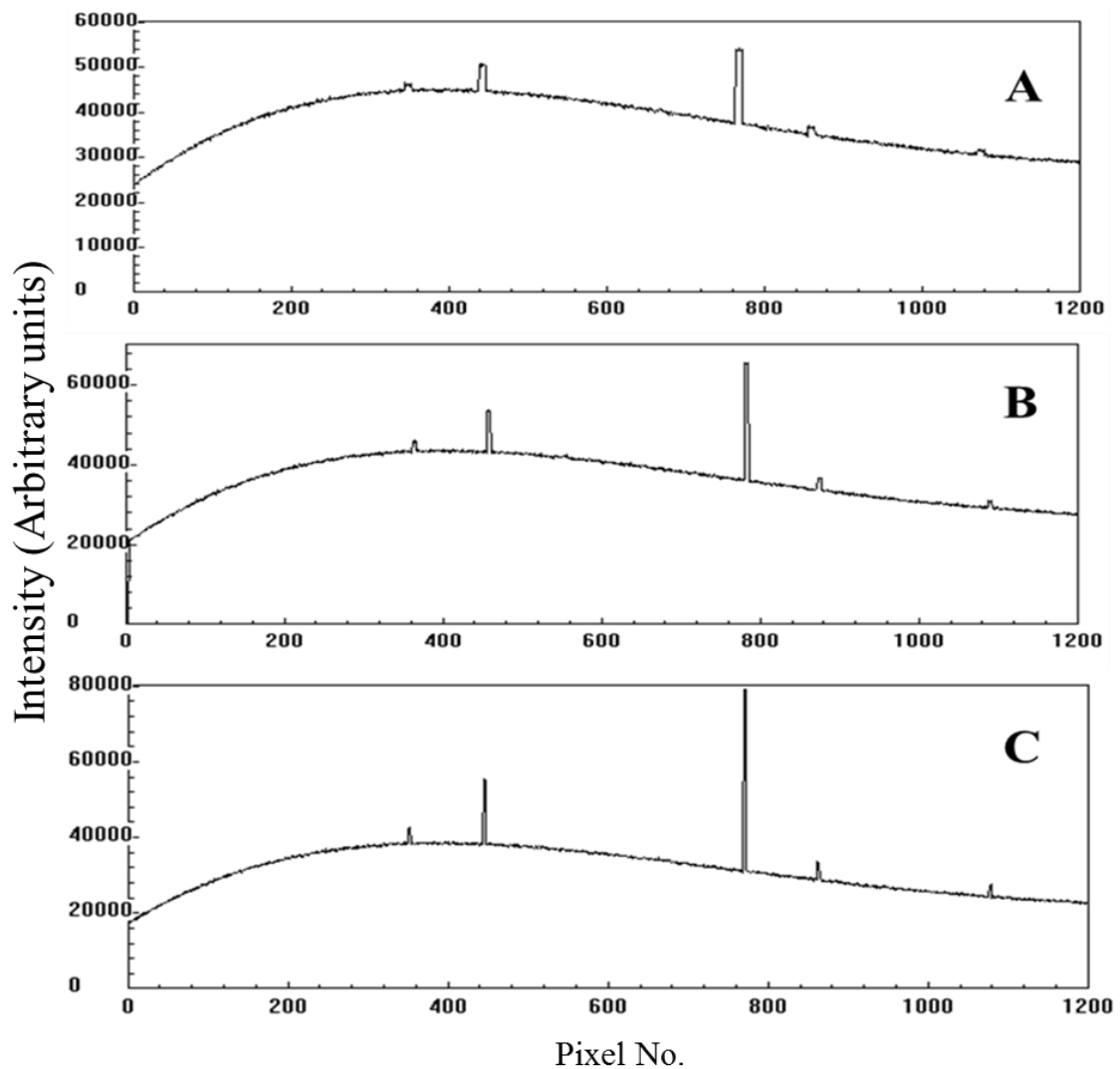


Figure 4.11: Plots A, B and C show the effects of varying the scale size of the optics convolution function from 3 to 9 respectively.

Figure 4.12 presents results from a simulation run that was used to determine the SNR achieved by an instrument operating under varying levels of ambient light. Five different optical resolutions were considered. The simulation was repeated for 2 different

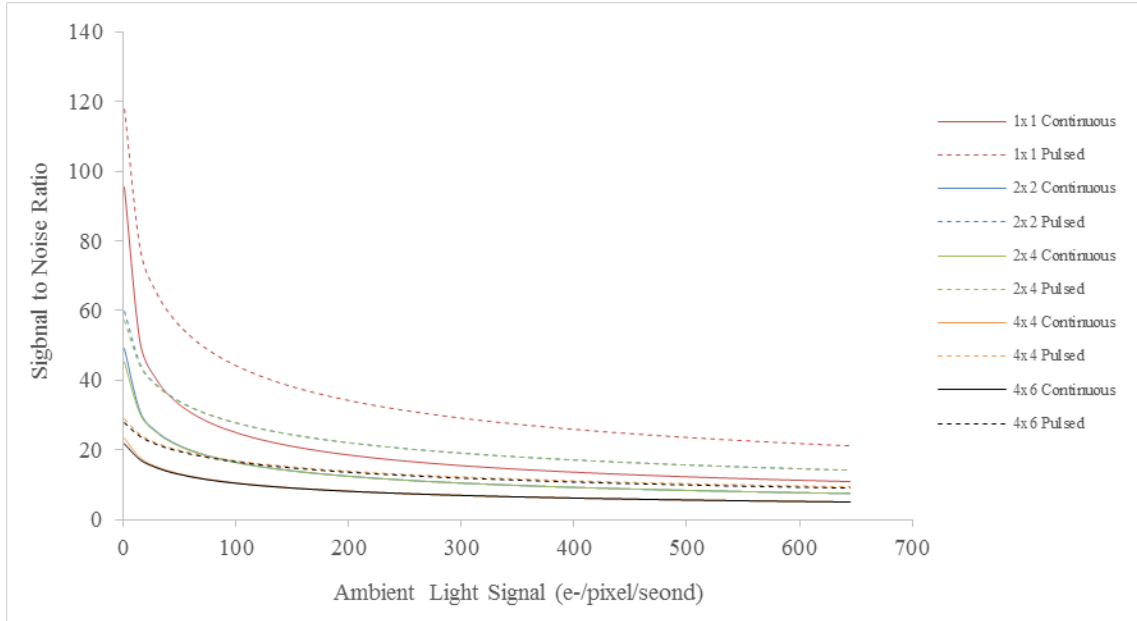


Figure 4.12: Variation in SNR value of the instrument as a function of the level of collected incident light. The dotted lines show the relationship when a pulsed laser is used within the instrument, while the solid lines show the SNR achieved when using a continuous laser. The plot shows how this relationship varies as the incident light is distributed over multiple pixels.

instrument configurations: a pulsed laser system and a continuous laser system (comparable to the simulation runs described in Section 4.2.1). In each scenario (indicated by the legend in Figure 4.12) the light was distributed over an increasing number of pixels and binned appropriately (in an identical process to the spectral extraction described in this section) but was not binned horizontally (as that would decrease the across order resolution).

Figure 4.12 shows that a clear increase in SNR is achieved when an instrument utilising a pulsed laser is used. This corresponds with the theory described in Section 4.2.1, which describes the effects of decreasing the frame time of a system while still integrating the same amount of signal (gained from a more powerful laser). The results from the SNR calculations in Section 4.2.1 are consistent with the spectral results presented above in that the SNR decreases as the signal is distributed over an increasing number of pixels.

The SNR analysis also suggests that if the Raman signal is distributed over many pixels, the effects of high ambient light have little effect, i.e. the SNR is low as a result of the reduced signal level, not because of increased noise. For example, at a background level of $15 \text{ e}^-/\text{pixel} \cdot \text{s}^{-1}$, the SNR level achieved by the instrument is 50 if the signal is focused into a single pixel (and 17 if the signal is distributed over 4×4 pixels). At a greater level of ambient light ($600 \text{ e}^-/\text{pixel} \cdot \text{s}^{-1}$), the difference between SNR values is reduced as the

light is redistributed. For signals focused into 1 pixel, the SNR is 11 while the SNR for light distributed over 16 pixels is 5.

4.2.3 OPERATING MODES: CORRELATED DOUBLE SAMPLING TECHNIQUES

In addition to reducing the effects of dark noise and the level of ambient light have on the system's SNR, it is important to optimise the readout process of the detector system. A key aspect of the readout sequence (and one that can introduce noise into the system) is the nature of the CDS process adopted. CDS, described fully in Chapter 2, is a method of sampling the data on the output of the CCD whilst limiting the bandwidth of the system. Specific CDS schemes are used to attenuate noise at both low frequencies and high frequencies. However, the optimum sampling scheme depends on the noise spectrum of the CCD and the clocking frequency required to achieve the science requirements of the instrument. Figure 4.13 provides an example of a typical CCD noise spectrum for a CCD output amplifier. The profile consists of a flat, thermal component usually referred to as white noise and a linear increase resulting from flicker noise. Flicker noise originates in the MOSFET of the CCD output circuit and its overall impact on the read noise depends on the time taken to read out a pixel (readout frequency). It should be noted that the thermal white noise does not increase with readout speed. In order to optimise the readout sequence, the software generates a noise spectrum based on input parameters such as the cut-off frequency of the MOSFET and the thermal properties of the circuit components.

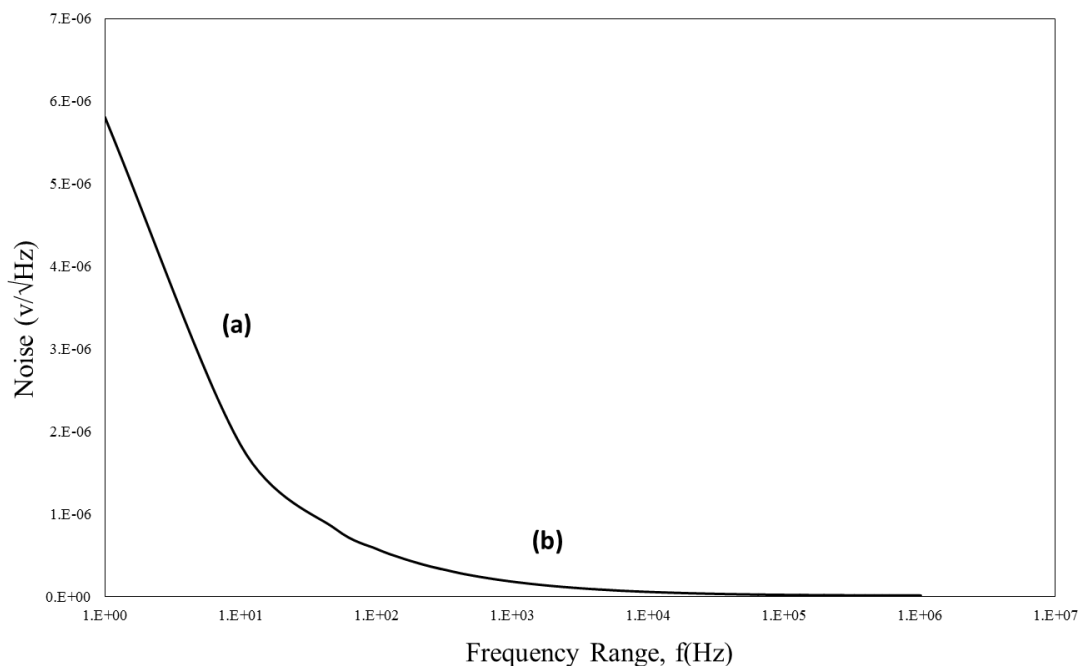


Figure 4.13: The noise spectrum for the output of a CCD. The plot was generated by the software simulation based on the known noise response of the MOSFET and the thermal properties of the output circuit. The spectrum has two components; 1/f noise (a) and the white noise (b).

Next, the simulation considers the response function of the adopted pixel sampling method. When matched to the readout sequence, the response function indicates which input frequencies are sampled effectively (the data) and which frequencies are filtered out (low frequency noise). Four different sampling schemes have been considered in the software simulations: DC restore and integrator, double delta, quad delta and dual slope integrator. Details of the sampling functions and how they vary with sampling frequency (readout speed) are given in Figures 4.14, 4.15, 4.15 and 4.16 respectively.

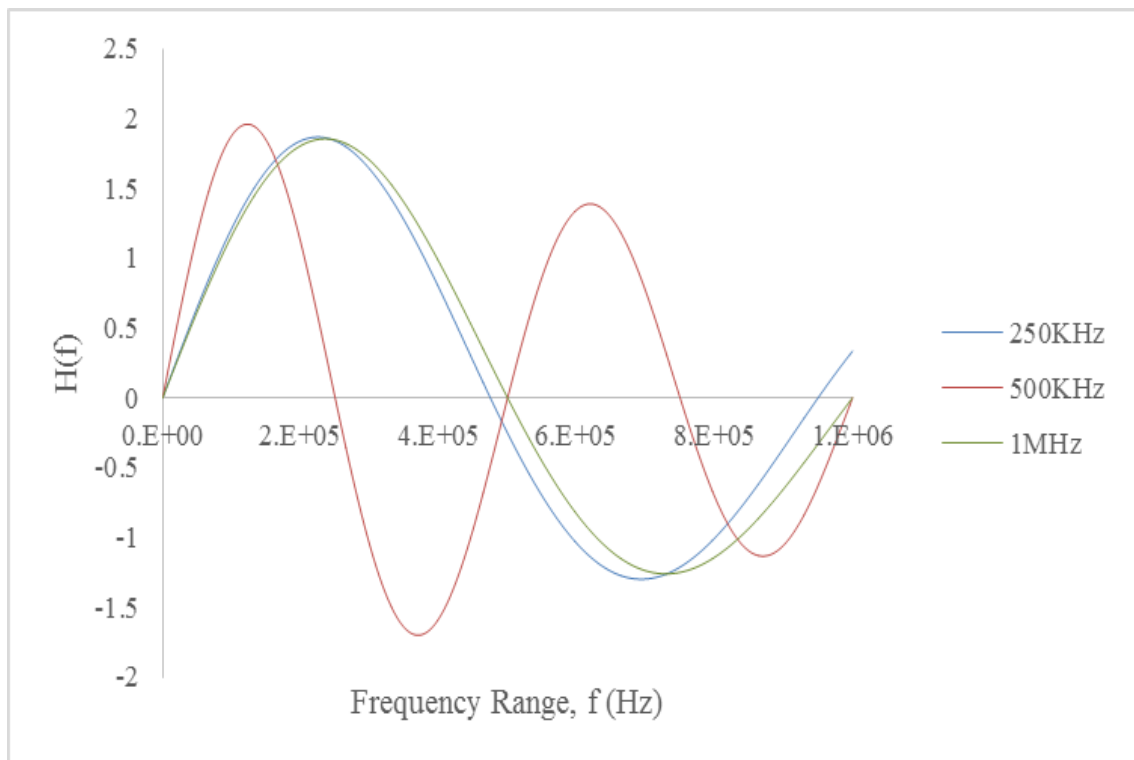


Figure 4.14: The double delta sampling scheme. The plot shows the frequencies which are filter (based on the negative or low amplitude of the function) and which frequencies are sampled (located at regions of high amplitude). The sampling function is given for three different sampling speeds to illustrate how the noise filtering can change depending on readout rate.

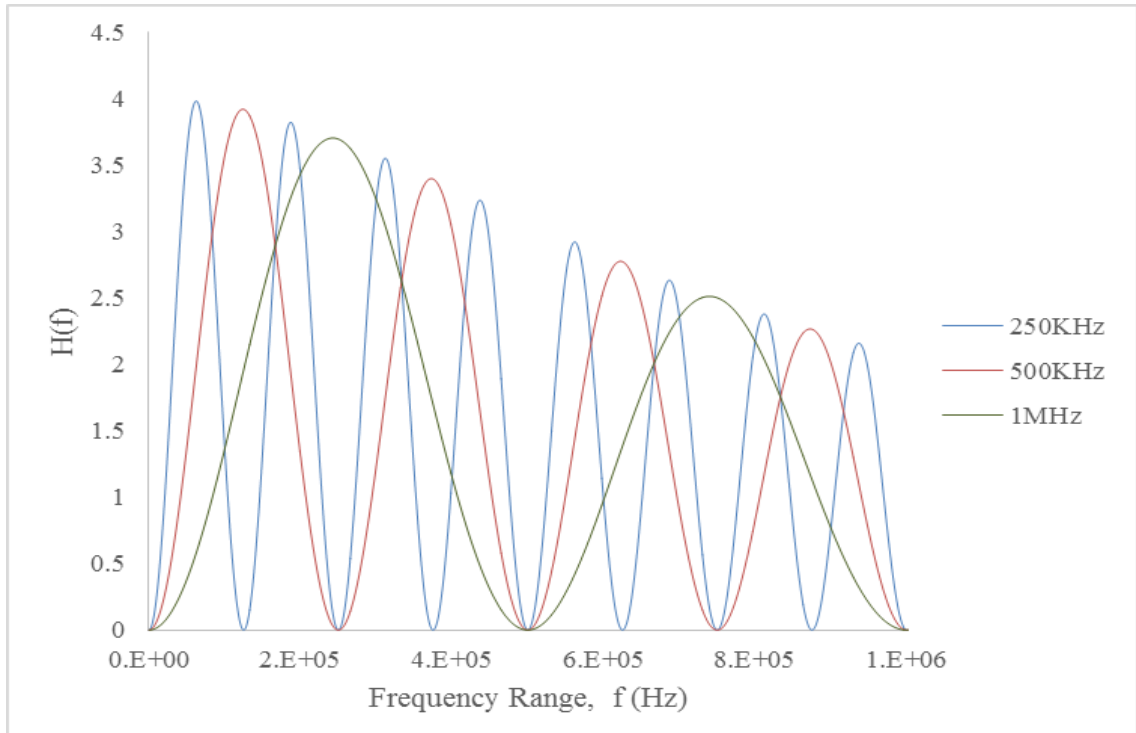


Figure 4.15: Response function for the quad delta sampling function over the frequency range of 0-1MHz at three different sampling frequencies.

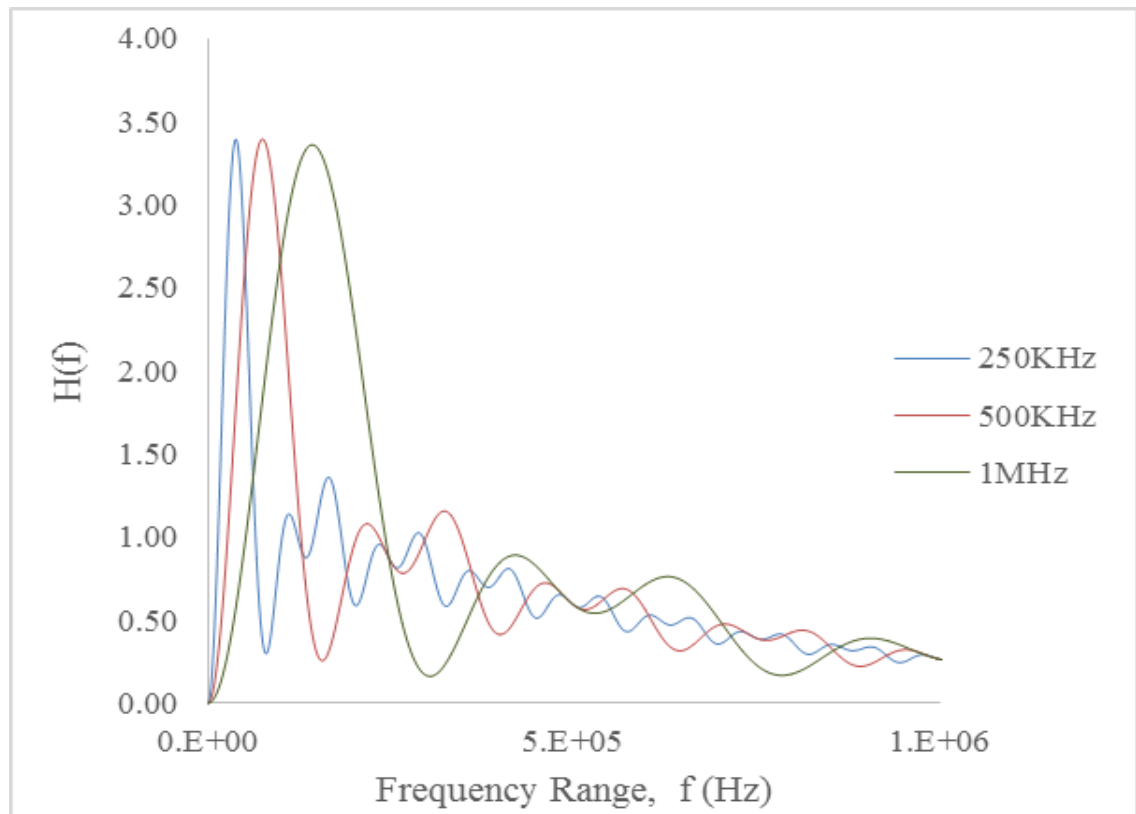


Figure 4.16: Dual restore and integrator response as a function of frequency.

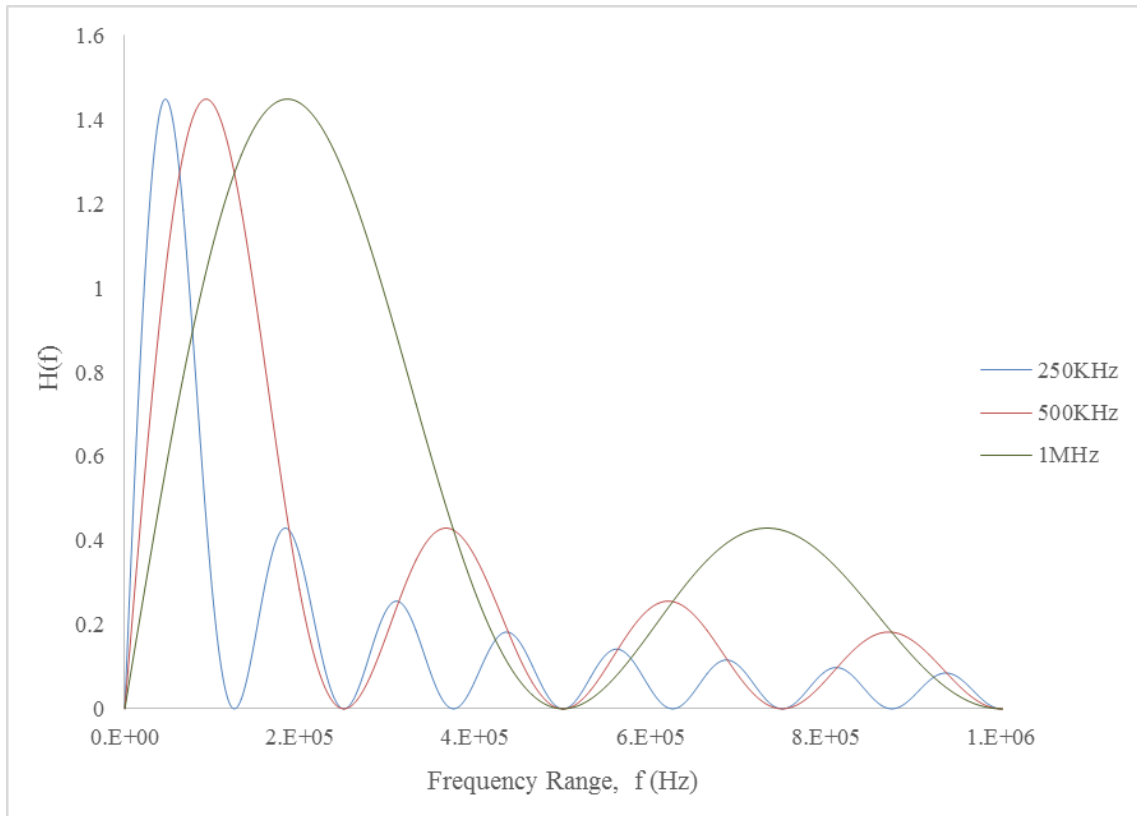


Figure 4.17: The dual slope integrator response function for 250KHz, 500KHz and 1MHz sampling frequencies.

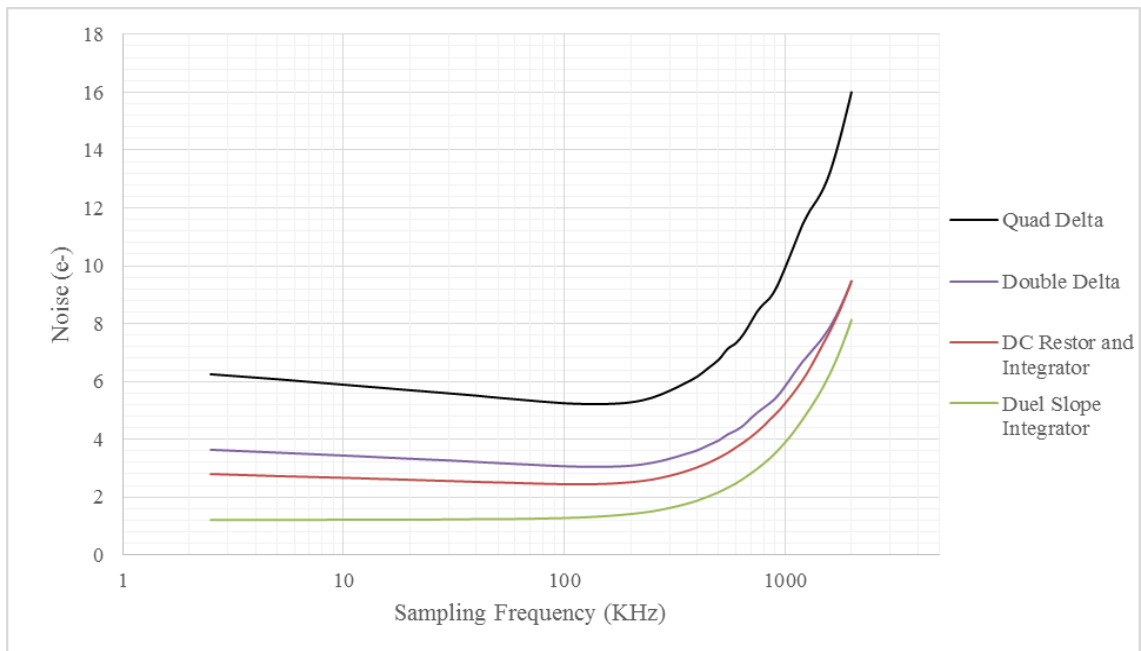


Figure 4.18: Comparison of the noise associated with each sampling scheme as a function of readout frequency.

Using the user defined sampling scheme and the noise profile of the CCD output circuit, the simulator calculates the noise associated with the CDS process using the formulae summarised by Hopkinson and Lumb (1982). This calculation was repeated for a large number of readout frequencies and for each CDS scheme to produce Figure 4.18. It should be noted that Figure 4.18 shows the noise functions for a CCD231 device which exhibits a responsivity of $>7\mu\text{V}/\text{e}^-$ (e2v technologies inc., 2009). From these curves, the simulation determines the appropriate level of CDS noise depending on the sampling scheme adopted and the readout speed required to achieve the scientific requirements. It is not always optimal to use the scheme which provides the lowest noise as the nature of the scheme may not be appropriate for the overall camera system. For example, the dual slope integration scheme provides the lowest noise over the entire frequency range, but it is inherently slow and may not suit a fast frame acquisition requirement.

4.2.4 OPERATING MODES: STACKING FRAMES

In addition to maximising the signal and minimising the noise in a system, acquired images are frequently stacked in order to increase the signal-to-noise ratio (the signal increases in proportion to the number of frames acquired, N , while the noise only increases by a factor of $\sqrt{N}$). However, with each additional frame there is also an increase in noise associated with the read noise level of the output FET on the CCD and the acquisition electronics. Consequently, it is important to consider exactly how much the SNR will change for any given system when frame stacking is implemented.

In order to investigate this issue in detail, the stacking process was simulated by calculating the SNR at a time, t , during the data acquisition process. The calculation assumed a constant Raman flux (around $2000\text{ electrons s}^{-1}$) and the parameters and properties of a back illuminated CCD47-20, operating in advanced inverted mode. Initially, it was assumed that the ambient light level was zero. The simulation ran from $t=0$ to the time taken to acquire 4 full frames. As the simulation progressed the signal and the dark current increased in accordance with the pre-defined rate until the illuminated pixel had reached full capacity (based on the CCD properties), at which point the frame was read out and a subsequent frame commenced integration. As the frame was read out the read noise was incorporated into the total SNR. This was also done for all subsequent

frames. The simulation was completed 8 times using two different read noise levels ($10e^-$ and $20e^-$) and for four different detector temperatures. Figure 4.19 shows how the SNR evolved with acquisition time for each of these scenarios.

At a detector temperature of 20°C , the curves shown in Figure 4.19 suggest that stacking frames does not significantly degrade the SNR of the acquired data, since the dark noise dominates over the read noise. In addition, the SNR difference between the $20 e^-$ read noise curve and the $10 e^-$ read noise curve at 20°C is minor, suggesting that stacking would have the same effect regardless of the read noise level at higher operating temperatures.

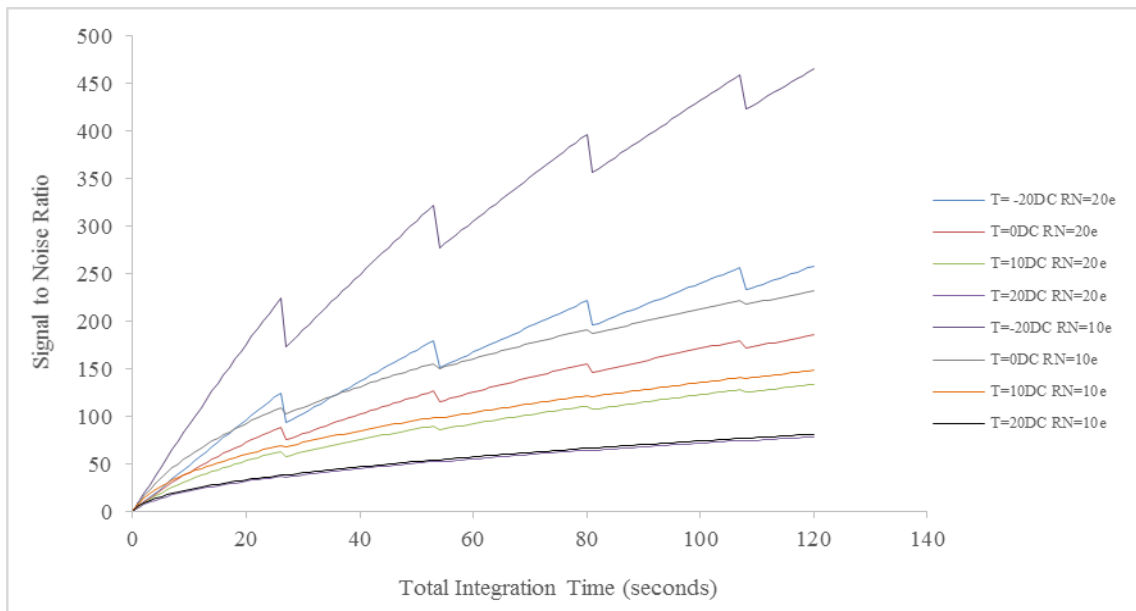


Figure 4.19: A plot illustrating how the simulated SNR value varies as a function of total integration time. The SNR has been calculated using four different dark noise rates (as a result of varying the detector temperature) and two different read noise levels.

As the temperature of the detector decreases and the dark noise level reduces, the impact of the read noise on frame stacking becomes clearer and significant drops in SNR are apparent in the plots of SNR versus time. At the signal and background rates considered here, the pixels reach full well capacity every 27 seconds, but to benefit from frame stacking (i.e. to increase the overall SNR) the subsequent frame should integrate for at least 9 seconds to image the SNR beyond what was achieved with a single frame.

Furthermore, the simulation was used to investigate the addition of a constant level of ambient light and a variable signal from either a pulsed or continuous laser. As stated earlier, a high powered pulsed laser can deliver a given amount of energy to the sample

in less time, meaning a pixel will reach full capacity sooner compared to a system utilising a continuous laser. In total, the simulation was completed for 3 different ambient light levels and for both systems. The SNR variation with integration time is shown in Figure 4.20.

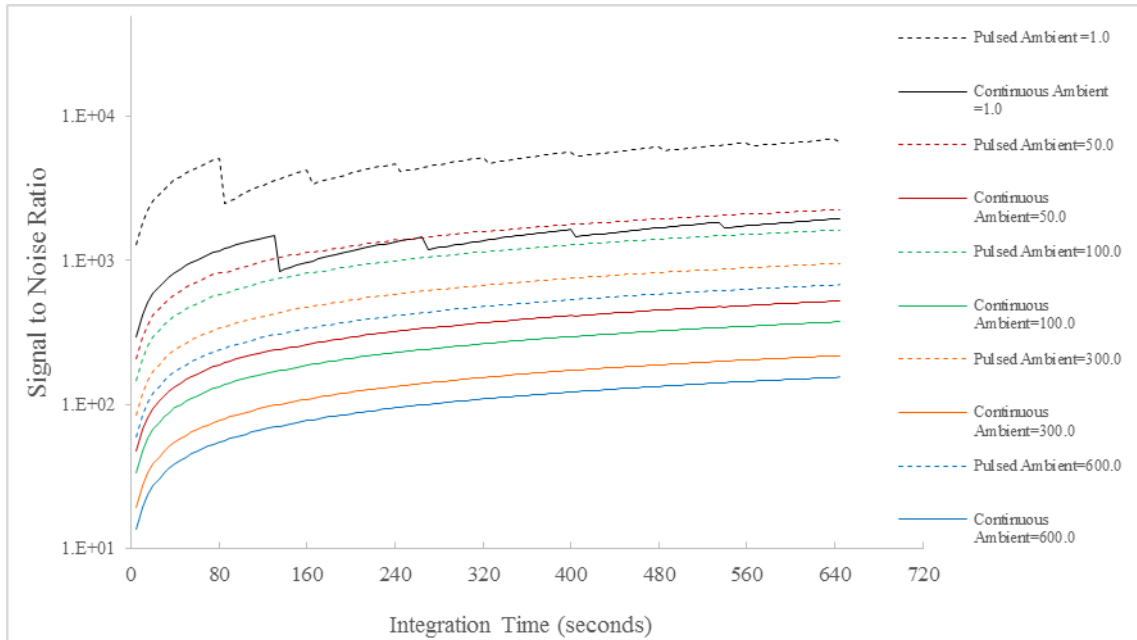


Figure 4.20: SNR achieved by the instrument as a function of total integration time. The maximum integration time for each frame is 79 seconds when using the pulsed laser (dotted line) and 133 seconds for the continuous laser (solid line). The relationship between SNR and total integration time is shown for three different levels of ambient light (the read noise was kept constant at $20e^-$).

Figure 4.20 illustrates that an instrument can achieve a much larger signal-to-noise ratio using a pulsed laser compared to a continuous laser. The difference between the SNR achieved using a pulsed laser and a continuous laser was ~ 500 at a high ambient light level (i.e. $600 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$) but as the ambient light was decreased the difference became larger. For example, at an ambient light level of $300 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$ and $1 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$, the difference between the pulsed and continuous systems was ~ 700 and ~ 5500 respectively.

Similarly, for the curves in Figure 4.19, the drop in signal due to additional read noise cannot be seen in high ambient light conditions (i.e. $600 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$). This is also true for signal levels of $300 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$. In fact, the negative impact of frame stacking does not become visible until the ambient light level is very low. At $1 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$ a reduction in SNR of ~ 2600 clearly occurs every 79 seconds for the pulsed system and a reduction of ~ 600 occurs every 130 seconds for a continuous laser system. At an ambient light level

of $50 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$ the SNR drop in both laser systems becomes less obvious. At the beginning of each frame, the SNR decreases by ~ 10 for the pulsed system and 4 for the continuous system. At an ambient light level of $100 \text{ e}^- \text{pixel}^{-1} \text{s}^{-1}$ an increase was observed in both the pulsed and continuous SNR curves at 79 seconds and 130 seconds. This increase is small (~ 4) compared to the increase in SNR observed at 78 seconds and 80 seconds for example, indicating that the frame stacking still had a negative effect on the SNR but of relatively small magnitude compared to the impact of ambient noise.

4.2.5 OPERATING MODES: DATA EXTRACTION

By fitting suitable polynomials to the dispersion order a spectrum can be obtained without including a large number of background pixels. The advantages of utilizing this technique are illustrated in Figure 4.21. The figure shows three separate spectra that were produced using an identical Flux Grid, featuring five of the most predominant bands commonly found in a beta-carotene spectrum, a high fluorescent background (usually observed in spectra from organic compounds) and a constant, low level of ambient light. The Flux Grid was integrated for 2 seconds and the entire Charge Grid was read out after 5 seconds.

Spectrum A shows a simulated beta-carotene spectrum extracted by enclosing the order in a rectangular box and vertically summing all pixels in each column within the box. This approach is preferred when the processing power is limited or if there is a risk that the order might change position during the operational lifetime of the instrument (i.e. the duration of a planetary mission). However, the box that incorporates the entire order will also comprise many pixels that only contain background noise leading to a reduction in the signal-to-noise ratio along the whole length of the spectrum.

Spectrum B illustrates the impact of using polynomials that do not encapsulate the entire order. The resulting ‘saw-tooth’ effect can be clearly seen across the full length of the spectrum. This demonstrates that an inappropriate data extraction method can produce artefacts which can, in turn, lead to an ambiguous/non-optimum spectral analysis.

Spectrum C was extracted using a polynomial that optimally surrounds the order (thereby minimising the number of background pixels incorporated in the final spectrum) whilst maintaining the integrity of the entire signal. There is a clear improvement in the spectral

SNR (compared with spectrum A) demonstrating the importance of optimising the data extraction method in order to improve the sensitivity limit of the instrument (a moving box algorithm can be used to determine the optimum envelope size to use for a given spectrometer configuration).

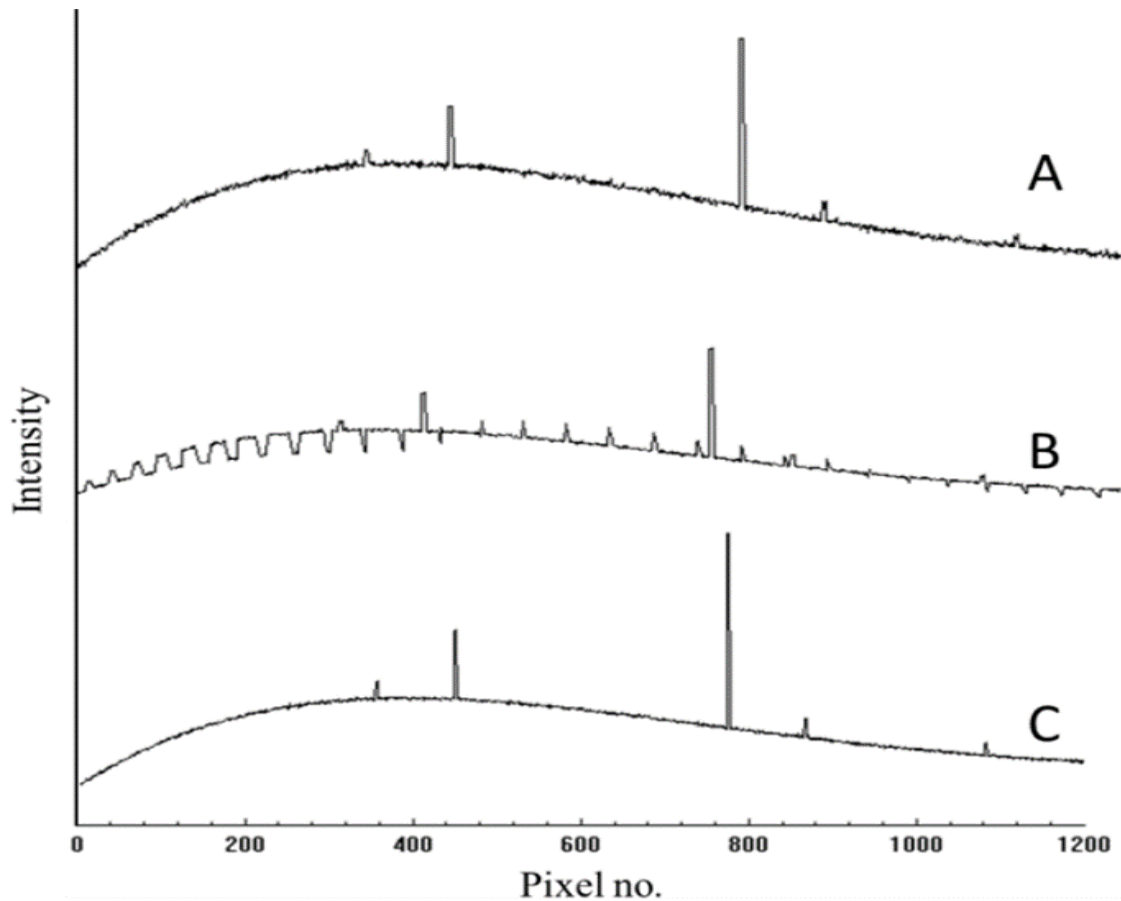


Figure 4.21: Effects of varying the data extraction method and demonstrates the importance of optimising each aspect of the system. The data in plot A was extracted using a large region of interest, plot B was produced by extracting the data using an ill-fitted polynomial and plot C displays data extracted using a well-fitted polynomial.

4.2.6 OPERATING MODES: MULTIPLE SPECTRAL ORDERS

Due to the severe mass and volume constraints applied to analytical space instruments, efforts have been focused on the development of a single instrument with the capability to perform multiple analytical techniques. Over the past decade, several combined instruments have been developed that are capable of performing LIBS in addition to Raman spectroscopy, such as SuperCam (described in detail in Chapter 1), which is due to be launched on the NASA 2020 rover, and the Raman/LIBS instrument originally developed for the ExoMars analytical suite (Ahlers et al 2008). Combined instrumentation relies on multiple techniques using shared instrument components. For example, both SuperCam and the Raman/LIBS instruments incorporate a single spectrometer and detector system that are optimised to distribute and detect both Raman photons and fluorescence photons emitted by the induced plasma. However, because of the larger spectral range of the plasma emission compared to Raman emission, LIBS instruments often utilise multiple spectral orders. Figure 4.22 shows the layout of the 11 spectral orders imaged by the Raman/LIBS instrument, courtesy of Ahlers et al 2008.

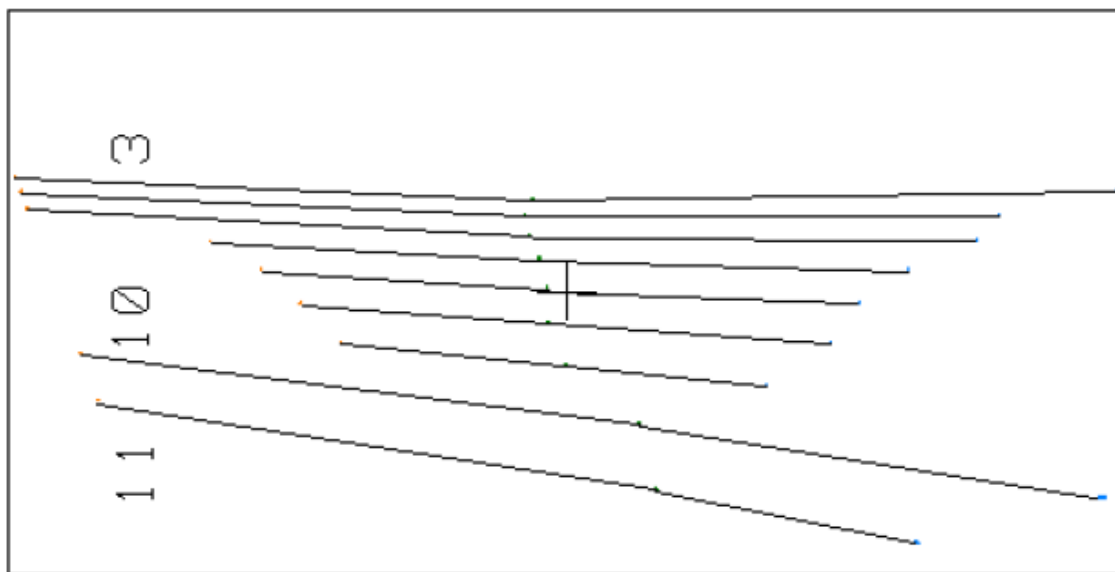


Figure 4.22: A schematic illustrating the position of the 11 spectral orders imaged by the detector within the Raman LIBS instrument. (Credit: Ahlers et al 2008).

Many Raman-only instruments, such as the MMRS instrument (described in Chapter 1, Section 1.3.4), also utilise multiple diffraction orders to increase the spectral range and resolution of the acquired spectra. Figure 4.23 shows a CCD image acquired using the MMRS instrument containing the distinctive emission bands of a neon calibration source. The neon bands are distributed over two diffraction orders with the lower and higher wavenumber emission lines appearing in the lower and upper orders respectively. The CCD image also shows evidence of ‘smear’ patterns extending from each emission band in the image. This pattern can arise when the instrument signal is continuously incident on the device, even during readout (i.e. the instrument does not use a mechanical or electronic shutter). It is evident from the image that the intense smear features interfere with the other spectral orders, adding in additional charge to pixels containing data from a different spectral region. The extent of the order contamination can be seen in the extracted spectrum (see Figure 4.24).

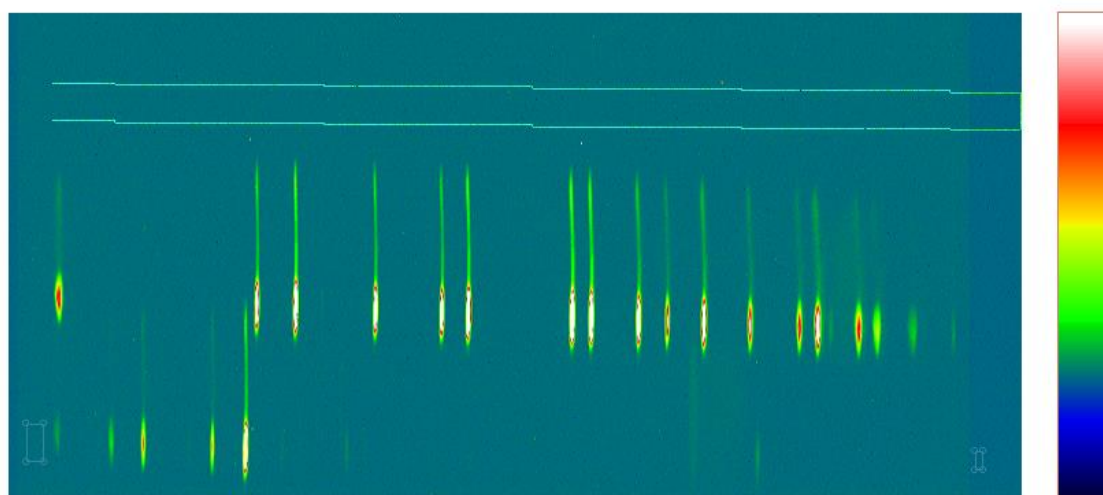


Figure 4.23: A CCD image of a neon calibration source acquired using the MMRS instrument developed by Washington University and JPL, in collaboration with the University of Leicester.

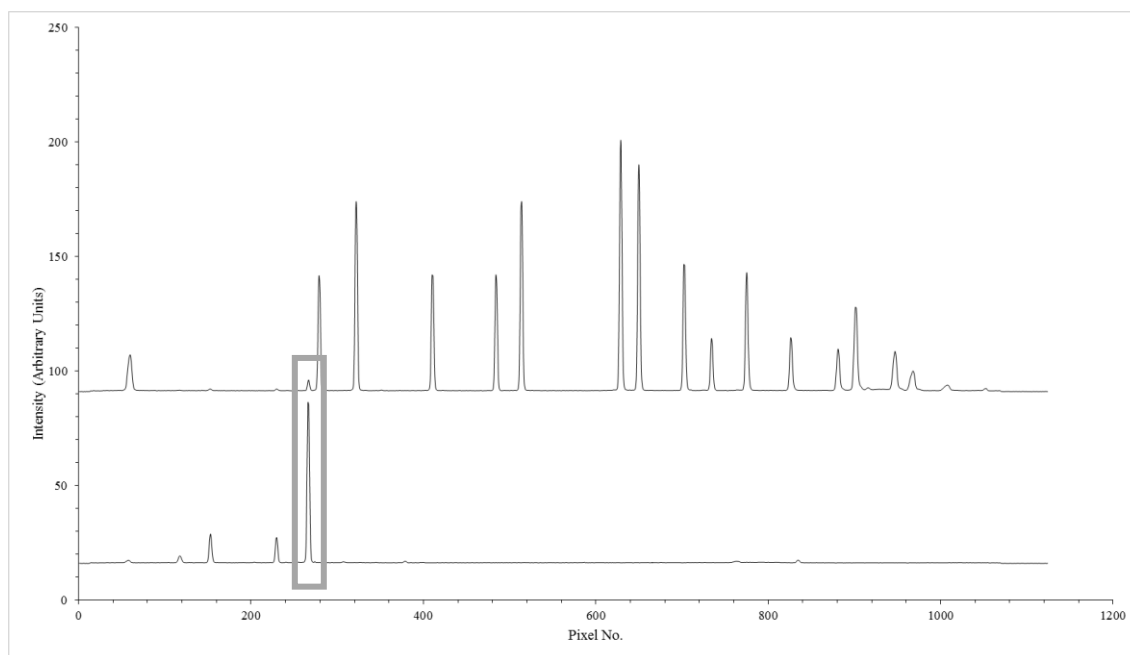


Figure 4.24: A spectrum extracted from the CCD image shown in Figure 4.22. The two spectral orders have been presented in parallel to show the effects of order contamination.

To simulate the performance of a combined Raman instrument (or a Raman-only instrument that utilises multiple diffraction orders), the software generates several different Flux Grids, each containing a separate diffraction order with uniquely defined spectral bands and fluorescence features. These grids are then stacked to create a master Flux Grid, which is used for all subsequent algorithms (including the integration of ambient light). Figure 4.25 shows a simulated CCD image containing three spectral orders, with each order containing several emission bands across the entire spectral range. The simulated CCD image in Figure 4.23 also contains the smeared effects seen in the CCD imaged acquired with the MMRS instrument. The degree of the contamination can be seen clearly in the extracted spectra shown in Figure 4.26. The CCD image was produced by simulating a pre-scan (see Section 4.1.2) - a 10 second integration time and a readout pixel rate of 250kHz. This operating mode and the high band intensities mean that every band featured in this CCD image has contaminated the other orders. Both Figure 4.24 and Figure 4.26 contain additional features that could be mistaken for weak spectral bands. Therefore, it is not only important to simulate combined or multi-order Raman instruments to evaluate spectral performance but to also understand the impact the operating mode can have on the quality of extracted data.

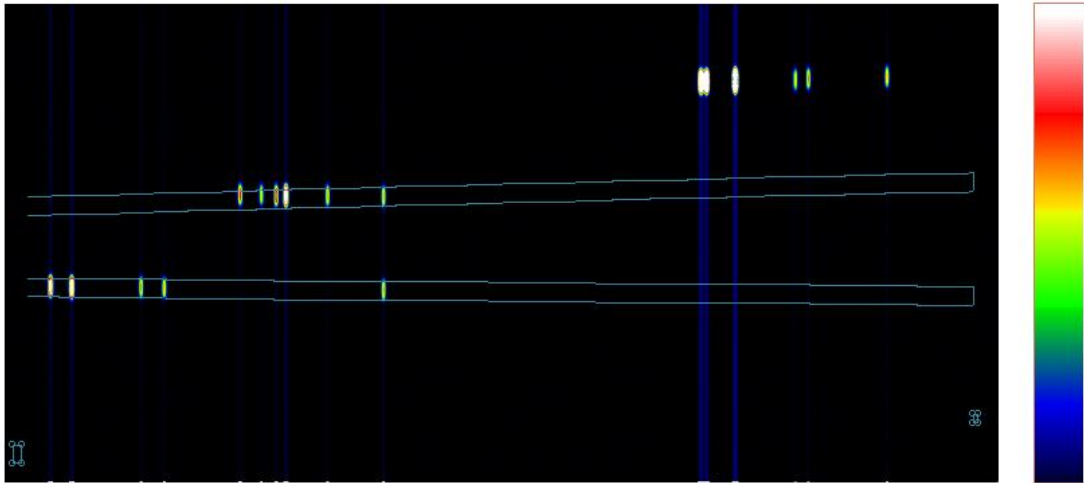


Figure 4.25: A simulated CCD image containing three diffraction orders.

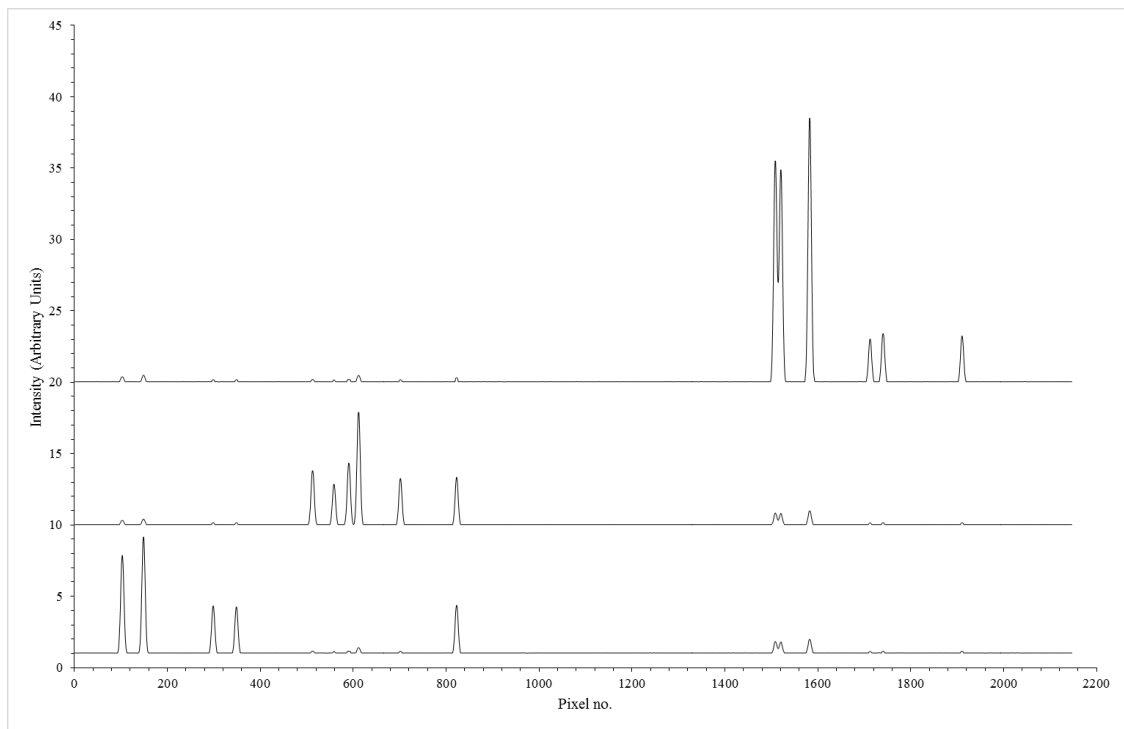


Figure 4.26: Data extracted from the three spectral orders in Figure 4.22. The spectra have been placed one above the other in the image to highlight how each peak has contaminated the other orders.

The impact of cross order contamination can be reduced by implementing a number of different approaches. For example, increasing the readout rate reduces the amount of time each pixel collects before it is read out. However, increasing the readout rate could increase the level of readout noise in the system. Alternatively, if the instrument utilises only two diffraction orders, and a CCD, multiple readout nodes, then the orders can be read out of the device in different directions (each towards a separate readout node). In this case the readout rate of the detector does not need to increase.

4.3 INSTRUMENT RECOMMENDATIONS

This chapter has described how the instrument simulator can aid in the design and performance optimisation process of an analytical instrument. Based on the results of the model, several instrument recommendations can be made for a challenging but realistic mission scenario: the deployment of a stand-off instrument or in situ Raman instrument, operating in high ambient light conditions (i.e. daytime).

Firstly, given the data presented in Figure 4.9 it is recommended that the laser energy does not exceed 0.1Js^{-1} at the sample surface. This limitation is the maximum amount of laser power that does not induce visible damage when interrogating organic material. Chapters 1 highlighted that many future missions will aim to find evidence of organic material on the surface of Mars and Venus (also see Chapter 6, Section 6.1), therefore it is important to restrict the laser energy to 0.1Js^{-1} to avoid damage to potential targets. However, 0.1Js^{-1} may not accurately reflect the damage threshold for all sample materials. Therefore preparatory work should be completed on expected samples in order to determine the upper laser energy limit for a particular mission.

Further to this, Figure 4.10 shows the effect that operating an instrument in particular levels of ambient light has on the SNR that can be achieved once the laser energy has been fixed (due to the limitations described above). The figure illustrates how increasing ambient light level decreases the SNR achieved by the instrument (i.e. if ambient light levels are greater than $220\text{ electrons pixel}^{-1}\text{ s}^{-1}$ then the SNR will not exceed 10)..

Figure 4.11 shows the effect that specific levels of dark signal have on a system operating in different ambient light conditions. In a high ambient light scenario, cooling a continuous laser instrument (with an inverted mode detector) to less than -20°C has only a small effect on the SNR (it will not exceed 10), since ambient noise dominates the system noise. At low ambient light levels, cooling the detector to -40°C does increase the SNR by a factor of 3. However, if the instrument is operating in daytime conditions, cooling the device to below -20°C , will use a relatively significant amount of power for a very small gain in SNR.

In the case of a pulsed laser instrument, a slightly larger SNR is achieved when operating at a detector temperature of -20°C , compared to the continuous laser system. However in high ambient light conditions, the performance is not dominated by dark signal levels

and, therefore, cooling to lower temperatures has no effect on system performance. It is therefore recommended that the detector is cooled to an optimum temperature such as -20°C (not necessarily a minimum temperature, such as -40°C) based on estimated ambient light levels.

Figure 4.11 illustrates the effect of distributing signal over a different number of pixels. It is evident from the plot that focusing the signal onto a small point on the surface of the detector, is optimum for instrument performance. However focusing a large signal in a small number of pixels can lead to pixel saturation.

To optimise the readout process and readout noise, some form of correlated double sampling technique has to be implemented. Figure 4.18 shows that using a dual slope integrator is the lowest noise option, in comparison to double delta, quad delta and Dual restore and integrator response. However, dual slope integrators are inherently slow, so if the system was required to perform a fast readout sequence (perhaps to synchronise with a pulsed laser) a quad delta sampling technique would give optimum read noise.

Frame stacking may be implemented to increase SNR levels once data has been retrieved by an instrument. However, Figure 4.12 shows how, in certain conditions, stacking frames can decrease the SNR achieved. For example, if the instrument detector has been sufficiently cooled so that dark noise is no longer the dominating factor, then the addition of read noise with each frame can significantly degrade the SNR. However, given the earlier recommendation to not cool the detector below -20°C in high ambient light levels, simulations show that stacking frames could have an overall positive effect on the SNR (given the relatively small decrease with each frame stack).

Figure 4.21 shows the effect that poor data extraction techniques can have on the quality of the data acquired. It is clear from the examples given in the figure that using a well-defined polynomial to extract data from the CCD image is crucial despite the additional processing required (compared to simply vertically binning pixels). The recommendation is therefore to use a polynomial ROI (fitted to the order distribution) where possible, but in scenarios where processing power is constrained, vertical binning within a window that minimally constrains those pixels that contain data should be performed in order to minimise noise.

Finally, this chapter also highlighted the effects of reading out a CCD that images many diffraction orders. The recommendation for optimising this process (by reducing signal contamination between orders) is to read separate parts of the device out through separate CCD outputs. However this may not reduce the contamination completely if the smallest independent section of the CCD image contains more than 2 diffraction orders. In this case the CCD should be read out at a frequency that minimises the contamination effects (or pseudo frame transfer operation should be implemented).

5 VERIFICATION OF RAMAN INSTRUMENT PERFORMANCE

The most advanced Raman spectroscopy systems currently being developed for planetary exploration were described in Chapter 1. It was also noted that the technique has recently been acknowledged to be a key tool in the future of analytical exploration of Mars, Venus, the Moon and potentially other bodies in the solar system, by various space agencies. Chapter 2 outlined the current state of technology available in the field of Raman instrument development (at a component level), and how each subsystem in a Raman instrument can be optimised for space exploration. Chapter 3 presented the development of a radiometric model, coupled with a pixel-level system simulation, which (as subsequently described in Chapter 4) can aid in the design and optimisation of a Raman system in an extensive number of configurations and mission scenarios. Following on, Chapter 5 describes a number of experimental campaigns that were used to verify the performance of each Raman instrument and a number of scientific studies in which the performance of the instrument was optimised using the various modelling tools that were described in Chapter 3 and Chapter 4.

The chapter firstly considers throughput measurements - a quantitative examination of the amount of light lost in the system, as a measure of potential instrument performance. Instrument throughput is especially important for systems measuring inherently weak signals such as Raman scattering and, as highlighted in Chapters 2, 3 and 4. Techniques such as stand-off Raman spectroscopy produce additional challenges in terms of signal detection.

It is also important to consider the detection limits of the instrument. These can be determined by modelling and measuring the system throughput at specific wavelengths. For example, the specific parameters of the filter partially determine the spectral range

and the low wavenumber cut-off point of the system, and will therefore establish the minimum wavenumber vibration that an instrument can detect. Detection limits cannot only be affected by subsystem transmission efficiencies, but also by the combination of components and the geometry of the system. For example, a specific combination of a diffraction grating and detector, in a particular geometry, can have an impact on the spectral range and resolution of the instrument.

The first section in this chapter describes the software environment created to enable end-to-end control of the laboratory (or field based) Raman spectrometer in order to collect data and verify the radiometric model.

This chapter then presents the throughput measurements of the RLS prototype instrument as well as a prototype stand-off instrument (developed as part of this PhD). The section also gives the outcomes of the radiometric model and comments on the limiting components and the impact that the throughput will have on the instrument performance.

The instrument performance is then assessed using the analysis of a terrestrial halite sample containing biomarkers using the RLS prototype instrument (described in Chapter 3, Section 3.1), and considers how such samples can be used to define the limits of instrument performance.

The following section of the chapter highlights the effects of larger working distances – a particular challenge for stand-off Raman instrumentation. The chapter presents spectra obtained with a stand-off prototype instrument and discusses the instrument performance achieved using different operating modes and hardware configurations (in order to ensure optimum performance).

Finally, the chapter discusses the effects of radiation damage on instrument performance and discusses (using the radiometric model presented in Chapter 3) instrument operations that can be implemented to reduce its impact. The section then describes two radiation damage campaigns that were completed at ESTEC in order to verify the effect of radiation damage on the CCD detectors.

5.1 THE SOFTWARE INTERFACE

To control and optimise the Raman instrumentation presented here, a user interface, referred to as the Instrument Control Environment (ICE), was developed. The ICE software was developed in the Microsoft Visual Basic Environment and is based on a multi-panel layout, with each panel containing the controls for each specific subsystem (as shown at the top of Figure 5.1). The software allows for data retrieval from several subsystems simultaneously, enabling the different trade-offs and complex relationships between instrument subsystems to be readily studied and optimised. The software provides fine control and manipulation of all instrument subsystems, allowing the acquisition of data at every stage/interface within the instrument, facilitating the verification of the subsystem models and simulation algorithms (see Chapter 4). Since its development, ICE has been used to control and optimise the Compact Integrated Raman Spectrometer (CIRS) developed by the Jet Propulsion Laboratory, the ExoMars Raman Laser Spectrometer Qualification systems (EQM), located at INTA in Madrid, and has been used in test procedures for the development of a UV camera system for ESA's Sentinel 5 spacecraft.

Figure 5.1 shows an aspect of the interface that controls the instrument's CCD detector and data acquisition system. The interface provides a method of readily altering

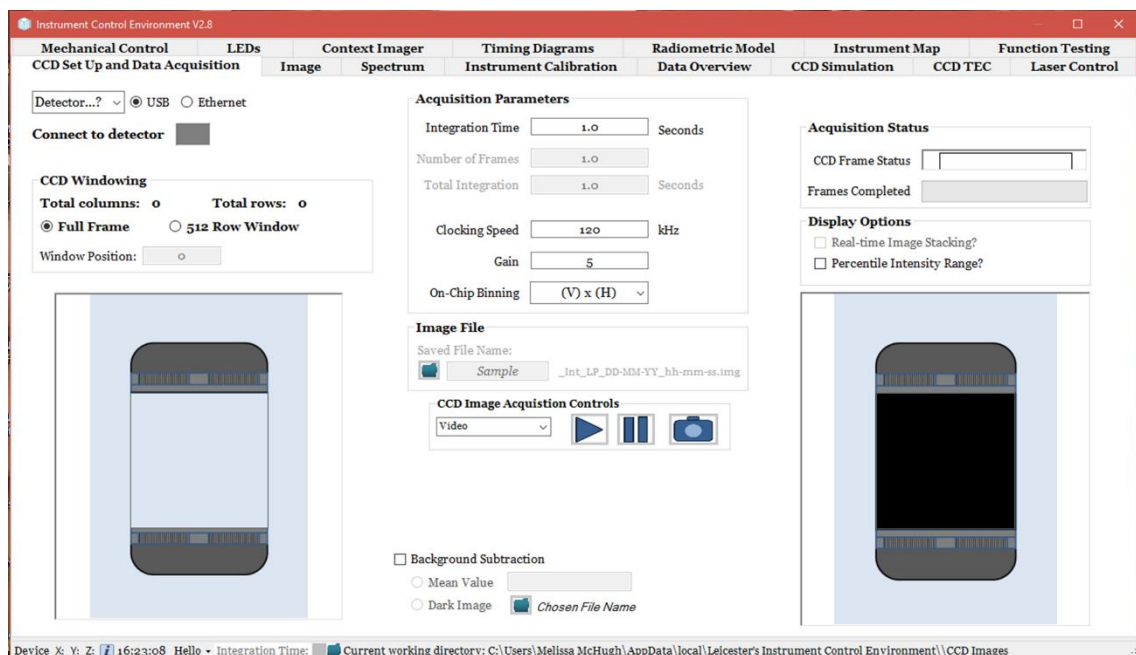


Figure 5.1: The CCD set-up and data acquisition panel within ICE.

parameters such as: the number of frames to be acquired, the total integration time, the frame time and CCD windowing (multiple windows can be used to surround several different dispersion orders). The panel also provides a method of operating the CCD in different operating modes, including single frame acquisition, shifting modes and a continuous frame acquisition mode to aid instrument focusing or alignment.

Figure 5.2 shows the ‘Image’ and ‘Spectrum’ panels within ICE. These panels provide the ability to perform and assess optimum data extraction and post-processing techniques

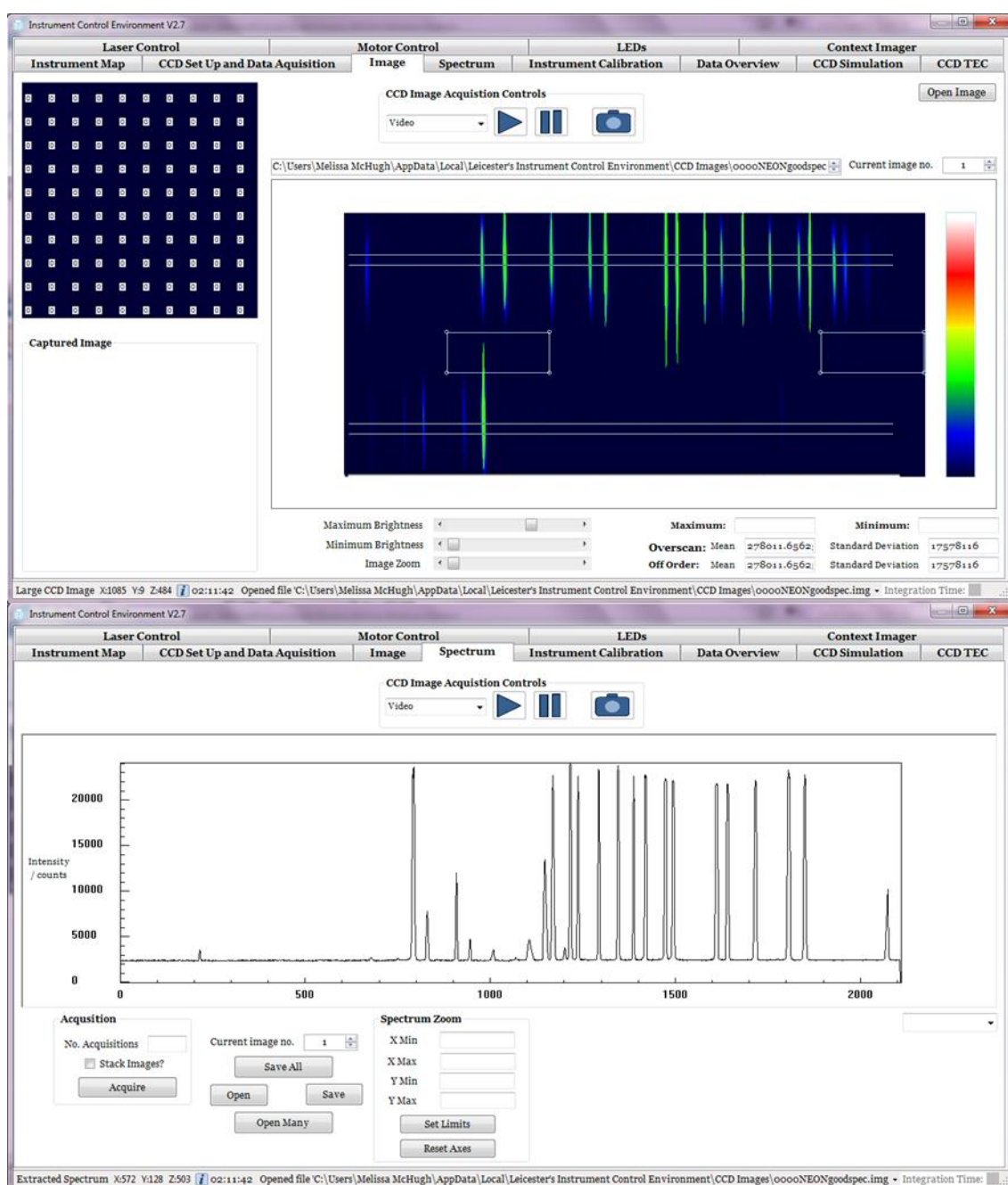


Figure 5.2: Top: The CDC image panel. Bottom: The Spectrum panel within the ICE software.

(such as those described in Chapter 4 Section 4.2) and investigate parameters such as noise on a pixel-by-pixel scale.

The software also features a 'Data Overview' panel (see Figure 5.3). It is this aspect of ICE that provides a fast and efficient way of not only optimising parameters based on real-time data, but also providing a view of the sample and therefore providing geological and mineralogical context to the data retrieved. The context imager is also coupled to an LED control panel (seen in Figure 5.4) which provides sample illumination (at both visible and UV wavelengths) in order to highlight areas of interest on the sample surface.

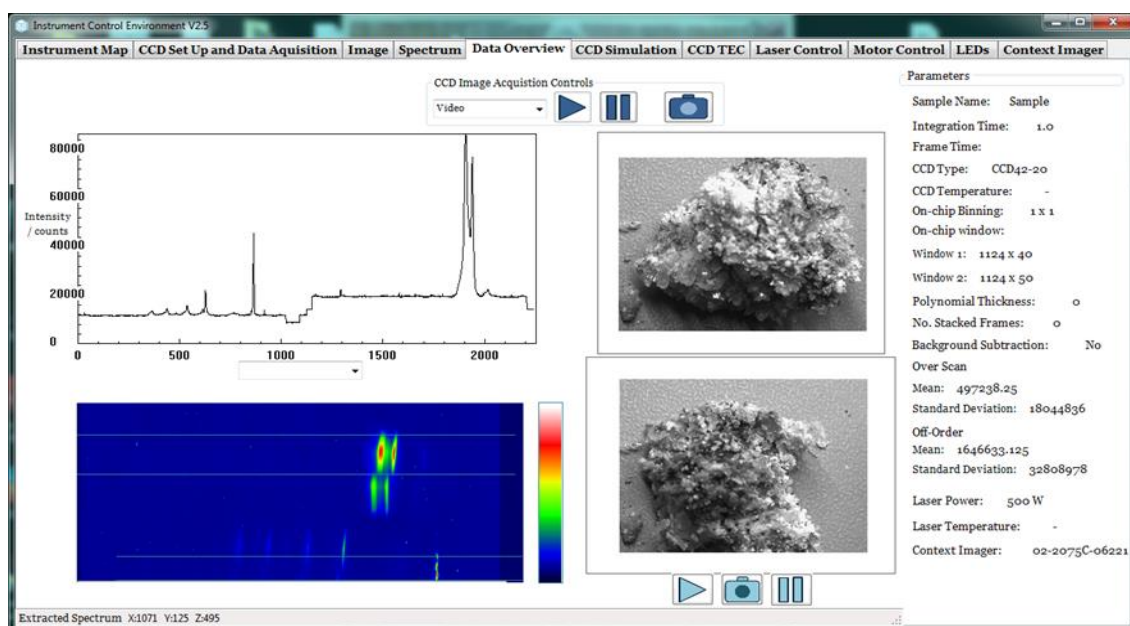


Figure 5.3: A screen shot of the 'Data Overview' panel.

The software environment also provides an interface to other hardware components in the system such as stepper motor's, which in turn can be used to move optical components (such as the telescope). Finally, ICE was used to control the thermal systems such as the detector and laser TECs in order to optimise and stabilise the systems. Thermal control procedures were completed using the software panels shown in Figure 5.5 and incorporated feedback control algorithms and temperature monitoring in order to ensure good levels of stabilisation).

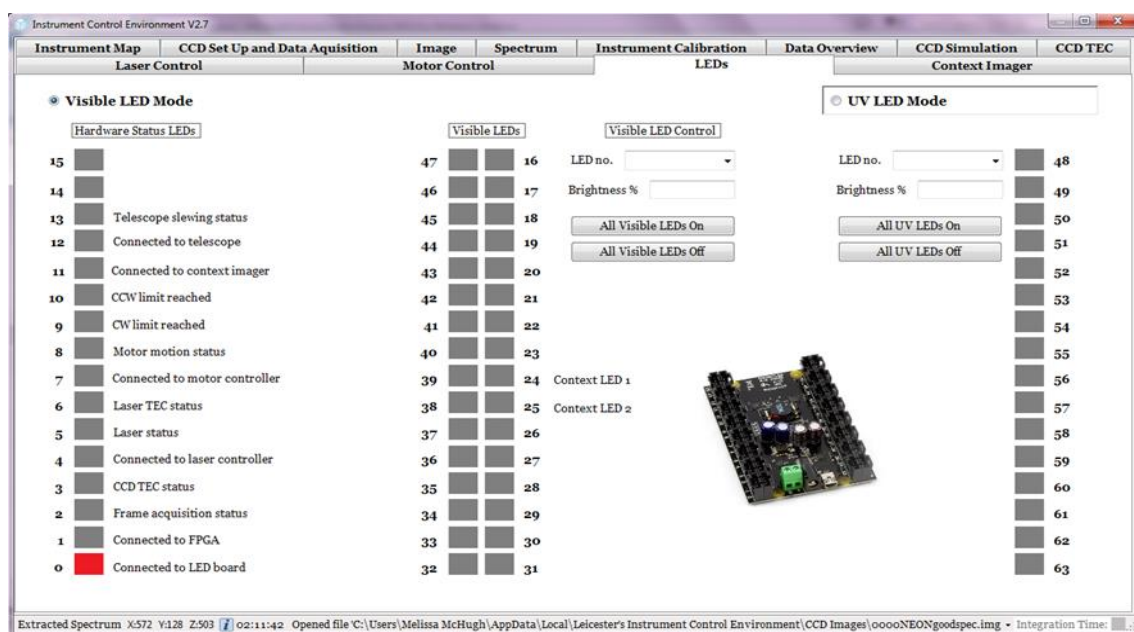


Figure 5.4: The LED control panel.

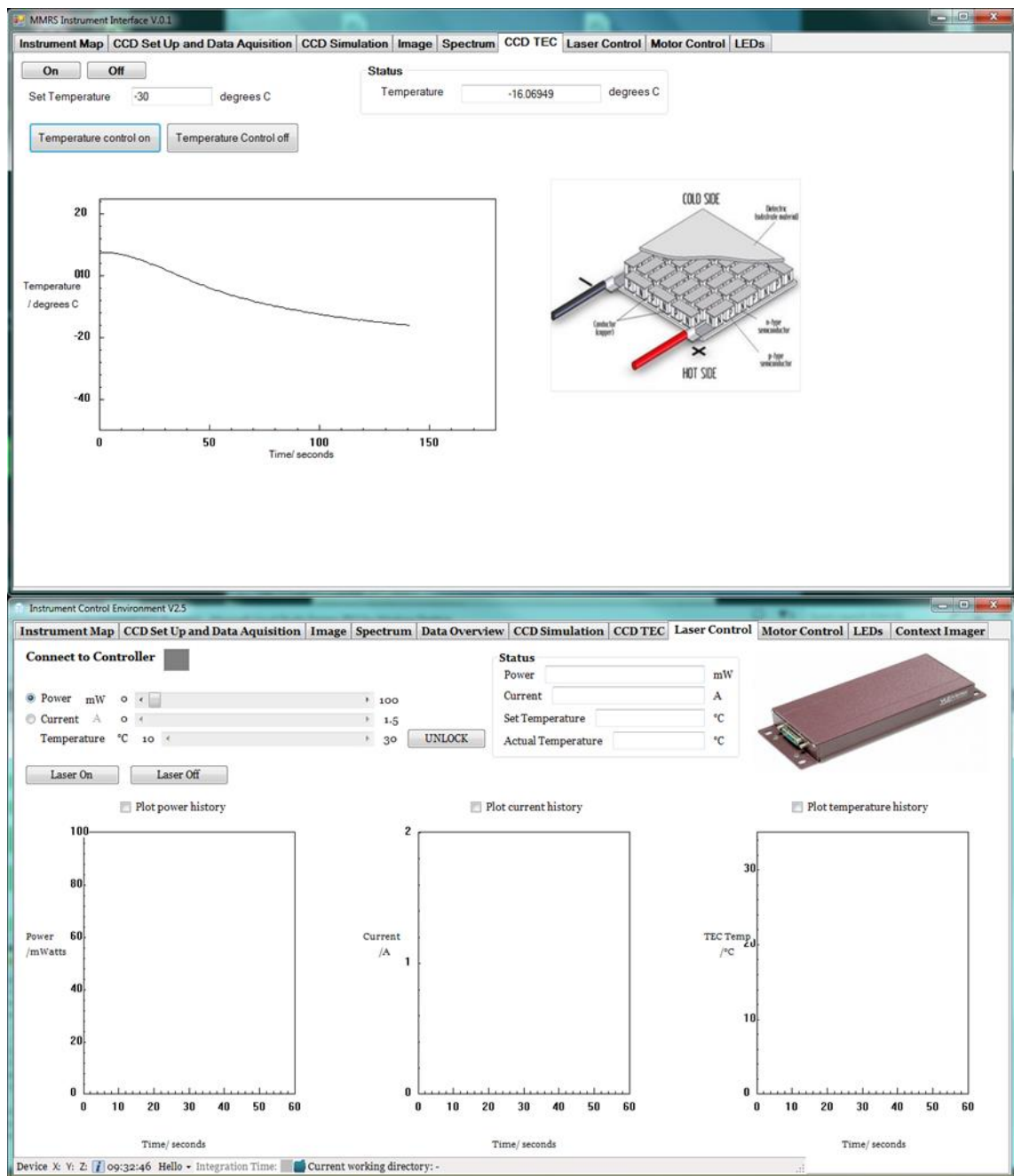


Figure 5.5: Top: The CCD TEC control panel and Bottom: The laser control tab.

5.2 INSTRUMENT THROUGHPUT

The throughput values presented for each component in this chapter were all measured using a 1936-R Newport power meter (see in Figure 5.6) and a 918D high performance photodiode sensor (also manufactured by Newport). For each component throughput measurement, the 918D detector was securely mounted in a position that measured the maximum input signal and ambient light level was subtracted from the signal detected. The detector was then remounted to measure the maximum signal transmitted by a component. The power meter accuracy is $\pm 0.2\%$ for continuous measurements and $\pm 1\%$ when operating in integration mode.

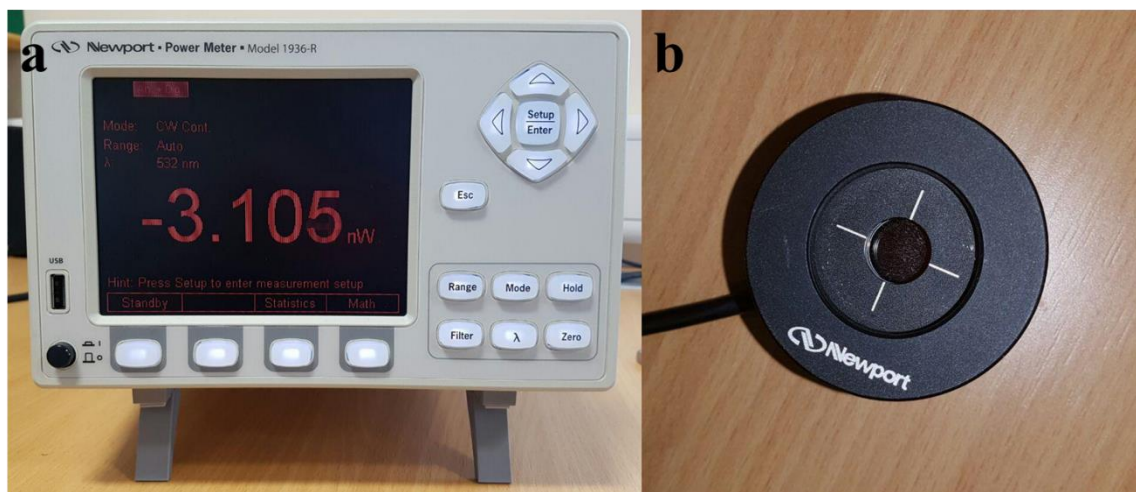


Figure 5.6: (a) a photograph of the 1936-R Newport power meter in continuous measurement mode and (b) is a photograph of 918D high performance photodiode sensor.

Where possible, a stabilised continuous laser (the Excelsior DPSS laser described in Chapter 3, Section 3.1.2) was used as the system input, as it provided an intense source of photons with which to accurately measure the magnitude of the signal loss, maximise measurement repeatability and provide a method of constraining the wavelength of the throughput. To prevent thermal damage to components, most measurements were acquired using a filtered laser beam. The filters varied in optical density from 0.1 to 4 depending on the component's damage threshold and efficiency. As a result, the throughput measurements are given as an overall percentage loss for comparison between system components and each measurement was repeated several times to obtain a measurement error. The percentage losses of each subsystem component are summarised in tables throughout Sections 5.2.1 to 5.2.4, with each table also containing a modelled throughput value (calculated using the algorithms presented in Chapter 3).

5.2.1 EXCITATION SOURCE AND OUTPUT OPTICS

This section presents the measured and modelled throughput values for the excitation source and output optics of the in situ RLS prototype instrument and the stand-off instrument described in Chapter 3.

IN SITU

Table 5.1 summarises the throughput measurements and signal losses for the excitation source and output optical components.

System Location	Input (μJ)	Output Average (μJ)	Output Measurement Error (μJ)	Measured loss (%)	Modelled loss (%)
Continuous Laser exit	100.0	72.3	4.1	27.7	0
Laser Launcher exit	67.3	62.5	1.5	7.1	3.0
Fibre 1	63.5	41.4	0.8	34.8	16.0
Optical head (Output Channel)	40.1	22.1	0.3	44.9	60

Table 5.1: A summary of the measured and modelled throughput measurements for the in situ RLS prototype using a 532nm laser.

The input signal for the laser power measurement is assumed to be the output quoted by the laser data sheet, which is 100mW. Therefore, the measured loss describes a performance difference compared to the expected emission. The continuous laser power was measured as $72.3 \pm 4.1 \text{ mW}$, which is 27.7% lower than the expected performance. It is possible that this is caused by debris between the diode and the output aperture as a result of operation in dusty environments (see Chapter 7). The semiconducting material also degrades over time, preventing the laser from producing its full 100mW of power.

The laser launcher contains a single lens and two fine adjustment mechanisms that move the fibre aperture into the focal point of the lens. The modelled throughput in Table 5.1 assumes that the throughput of the launcher is solely determined by the throughput of the

lens. However, if the optical fibre aperture and the lens are not NA matched then light will be lost from the system and this could be the cause of the 7% decrease in throughput compared to the modelled 3%.

Table 5.1 shows that optical fibres 1 and 2 reduce the throughput of the system by 35% and 12% respectively. The modelled radiometric model accounts for internal fibre losses as well as aperture misalignment (through NA mismatching). However, it does not include the effects of internal damage caused by extensive bending (for example). Therefore, it is likely that the additional loss observed in optical fibre 1 is caused by a large degree of internal damage.

As shown in Figure 3.10 in Chapter 2, the M-10X optical probe head contains two diverging light paths, separated by the notch filter. Table 5.1 shows the measured and modelled throughput of the output channel, i.e. the path the laser light takes from the fibre aperture to the sample. The laser light reaches the sample via a notch filter, which transmits only a small range of wavelengths centred on 532nm.

The modelled loss in the optical fibre is described as a ‘worst case’ scenario and is derived from lens throughput, notch filter transmission efficiency and the loss expected through extreme fibre misalignment. The measured throughput exceeded the modelled loss by ~15%, and it can therefore be assumed that the fibre alignment is an improvement on the configuration described by the data sheet. However, it is reasonable to assume that the filter and the lenses have transmission efficiencies in excess of 90%, so ~30% of the losses measured could still be from misalignment.

STAND-OFF

Table 5.2 presents the measured and modelled light losses of each component in the stand-off Raman spectrometer laser and output optics system. The laser excitation source was a Surelite I Nd: YAG 532nm laser that produced 5ns pulses at a repetition rate of 10Hz. Due to the nanosecond time scale duration of the laser pulses (see Figure 3.22), the energy per pulse was derived by integrating emitted laser pulses over a 20 second time.

Output measurement errors are, on the whole, larger than those measured for the continuous laser. It is assumed that this is a result of using the integrating mode operation, which is accurate to $\pm 1\%$ of the signal, compared to the $\pm 0.2\%$ accuracy in continuous mode.

System Location	Input (μJ)	Output Average(μJ)	Output		
			Measurement Error (μJ)	Measured loss (%)	Modelled loss (%)
Pulsed Laser	71.0	68.04	6.23	4.17	0.0
After Beam splitter	68.0	60.13	3.67	11.6	1.5
After Two lenses	71.0	69.77	2.29	1.74	1.5
Distance of 1m	71.0	69.80	0.18	1.70	1.5

Table 5. 2: A table to show the measured and modelled throughput losses as a percentage of the component input in the stand-off Raman spectrometer

The beam splitter measured loss was a factor of 10 larger than the predicted loss. The purpose of the beam splitter is to redirect a significant fraction of the 1064nm photons generated by the laser in addition to the 532nm photons. Without the beam splitter many of the photons ejected from the laser would be detected and measured as 532nm photons and this was likely to be the case during the measurement of the beam splitter input. Assuming the modelled efficiency of the beam splitter accounts for reflection and absorption of 532nm photons, a decrease of 11% indicates that $\sim 10\%$ of the original beam exiting the laser was composed of 1064nm photons.

Table 5.2 also shows that the two lens focussing system (implemented to focus the laser beam over distances in the range 30cm to 5m) reduces the throughput of the system by $1.7 \pm 2.3\%$. The modelled value of 1.5% was based on transmission efficiency only, but is within the error range of the measurement, suggesting there were no losses in the system due to misalignment. In addition, the results show that there was no detectable loss when

measuring the throughput at a distance of 1m. This implies again that the light was sufficiently focused throughout the system.

Overall, the model and the throughput measurements suggest that very little light is lost in the stand-off laser output system in this particular co-axial configuration.

5.2.2 INPUT OPTICS

Input optics are required to maximise the amount of Raman emission collected, while rejecting the maximum amount of Rayleigh scattered light (a much more intense scattering process that can obscure the relatively weak Raman emission). This section presents the measured and modelled throughput of the input optical system for both the in situ instrument and stand-off instruments.

IN SITU

As described in Chapter 3, the in situ collection optic is composed of an M-10X optical probe head. The probe head, shown in Figure 3.10, has two apertures at the top of the tube (an input and output aperture) each leading to two separate optical paths that converge at the bottom of the probe head after passing through the notch filter.

In the first instance, a 532nm input light source was directed into the optical head aperture and into the shared optical path. The detector was positioned such that it would measure the emission from the output channel at the top of the optical head (i.e. the aperture that directs the Raman emission into the fibre). By using a 532nm light source, this measurement quantifies the amount of elastically scattered light that is transmitted by the notch filter.

The measurement shown in Table 5.3 confirmed that the notch filter does reduce the collected 532nm light by $99.995 \pm 12.3\%$ (the model expected 99.992 % of 532nm light entering the optical head to be rejected by the notch filter within the probe head).

The second set of measurements were taken using a neon calibration source (described in Chapter 3 section 3.1.7) to simulate inelastic scattering within the sample, i.e. emission with a wavelength $>532\text{nm}$. With the photodiode detector positioned to measure the transmission through the notch filter, the losses were measured at 40%. Losses resulting

from the use of an optical fibre for coupling the optical head to the spectrometer are given in Table 5.1.

System Location	Wavelength (nm)	Input (mW)	Output Average (mW)	Output Measurement Error (mW)	Measured loss (%)	Modelled loss (%)
Optical Head (Input Channel)	532	26.1	1.3×10^{-5}	1.6×10^{-6}	99.995	99.992
Optical head (Input Channel)	633	0.079	3.2×10^{-5}	7.1×10^{-8}	40.4	60.0

Table 5.3: A summary of the throughput measurements of the optical head.

STAND-OFF

To measure the loss in the system due to the Mead ETX-125 Maksutov-Cassegrain telescope, an LED, with an irradiance of Radiance $47.62 \text{ W m}^{-2} \text{ sr}^{-1}$, was placed at a distance of 3.6m away from the telescope. The 918D photodiode sensor was mounted to the telescope exit aperture in order to measure the intensity of light transferred through the component. Table 5.4 shows the loss measured and estimated for the telescope and the lens focusing the input light into the system's optical head.

System Location	Input (mW)	Output Average (mW)	Output Measurement Error (mW)	Measured loss (%)	Modelled loss (%)
Telescope	117.18	215.6	0.22	1.84	1.90
Lens	95.02	85.60	0.26	9.91	3.0

Table 5.4: Throughput losses in the system due to the telescope collection power and the focusing lens.

The modelled throughput loss of the telescope was measured at $1.84 \pm 0.1\%$. This is a factor of 0.97 lower than the predicted measurement, indicating that the model accurately accounts for each factor effecting the efficiency of the telescope collection optics and could be used to predict signal loss at a stand-off distance (see Chapter 7, Sections 7.2.6 and 7.3.6).

The throughput loss due to the lens was measured to be larger than that predicted. It is due to misalignment (vignetting may occur) or the transmission efficiency of the lens has decreasing, due to damage to the lens.

5.2.3 SPECTROGRAPH

Table 5.5 summarises the measured throughput of each of the spectrograph components. The measurements were acquired by directing a filtered laser beam of known intensity into each component of the spectrometer and measuring the exiting beam. The overall loss in the spectrometer was measured by sending a beam of known intensity through the spectrometer, with each component appropriately aligned. In the case of the diffraction grating, the modelled loss is based on the grating transmission efficiency in addition to the redirection of light into separate diffraction orders.

For each component, the measured loss is greater than the modelled loss. For example, the predicted loss for the collimator was 10%. However, the measured loss was considerably larger at $44.8 \pm 2\%$. The additional loss is likely to be due to debris or dust on the surface of the lens, since the lens is secured to an optical plate to prevent misalignment. However the unit has been subject to frequent transportation (see Chapter 7), which could have unaligned one of the several lenses comprising the component. The loss measured for the collimating lens is also large in comparison to that of the camera lens, which was $14.3 \pm 2\%$. This loss value is closer to the expected loss of 10% predicted by the model.

The signal loss due to the diffraction grating at the zero order position and first order position is $85.41 \pm 11.2\%$ and $76.1 \pm 11.3\%$ respectively. The predicted value for the first order (the diffraction order containing the Raman emission) of 70.0 is within the error of the measured value.

System Location	Input (mW)	Output Average(mW)	Output	Measured loss (%)	Modelled loss (%)
			Measurement Error (mW)		
Collimator	37.0	20.4	0.60	44.8	10.0
zero order diffraction	20.4	2.98	8.37×10^{-2}	85.4	70.0
first order diffraction	10.2	2.44	0.270	76.1	70.0
Camera lens	4.88	4.18	0.11	14.3	10.0
Spectrometer end-to-end	29.0	8.27	0.11	71.5	75.6

Table 5.5: A summary of the throughput measurements for each spectrograph component and the spectrograph as a whole.

The overall measured loss of the spectrometer is $71.5 \pm 1.3\%$. The predicted value of 75.6% is slightly larger but not within the error of the measured amount. The additional signal (that results in a lower than predicted loss) could result from a change in ambient light levels during the measurement, which would create an offset in the measured signal.

5.2.4 DETECTOR

This section describes the tests performed to verify the performance of the CCD42-10 detector system. These performance tests were not only completed for model verification but also to verify the performance of the RLS detector system (in collaboration with INTA). The output of the model was verified by illuminating the CCD system with a source of known intensity and using the digital data from a captured image to verify the estimated resulting ADU values. Table 5.6 shows a number of known system parameters used to estimate a system response.

Using the equations presented in Chapter 3, Section_ and the values listed in tables_, the CCD response after amplification was calculated to be $9.90\text{E-}06 \text{ V/e}^-$. Since the system uses a 14-bit digitisation range, the ADC resolution equates to 0.00024 V/ADU or 24.66 e-/ADU . This implies that the ADC will saturate (reach an ADU value of 16384) at a charge level of 404k electrons.

Table 5.6: A summary of the detector system parameters.

Parameter	Value
Characteristic	Value
Detector Responsivity	3.30E-06 V/e-
Amplifier Gain	3
FW Capacity	380000 e-
ADC Digitisation Maximum	16384
ADC Voltage Range	4V
QE	0.9

To verify this value, a laser spot was focused onto the surface of the detector. This was achieved using the Excelsior DPSS laser, the M-10X laser beam launcher, an optical fibre and the MultiRxn Probe optical head (see Chapter 3, Section 3.1.2 for a full description of each component). The laser light intensity was reduced to a level only just capable of saturating the detector at the surface of the detector using a $\sim 1\text{mm}$ pinhole and several neutral density filters (also described in Chapter 3, Section 3.1.2). The intensity was measured using the 1936-R Newport power meter described in Section 5.2. The use of a pinhole also constrained the incident signal to a 20×20 pixel area on the detector. Figure 5.7 shows a (just) saturated CCD image containing the laser point, acquired with an integration time of 1s (using the ICE interface described in Section 5.1).

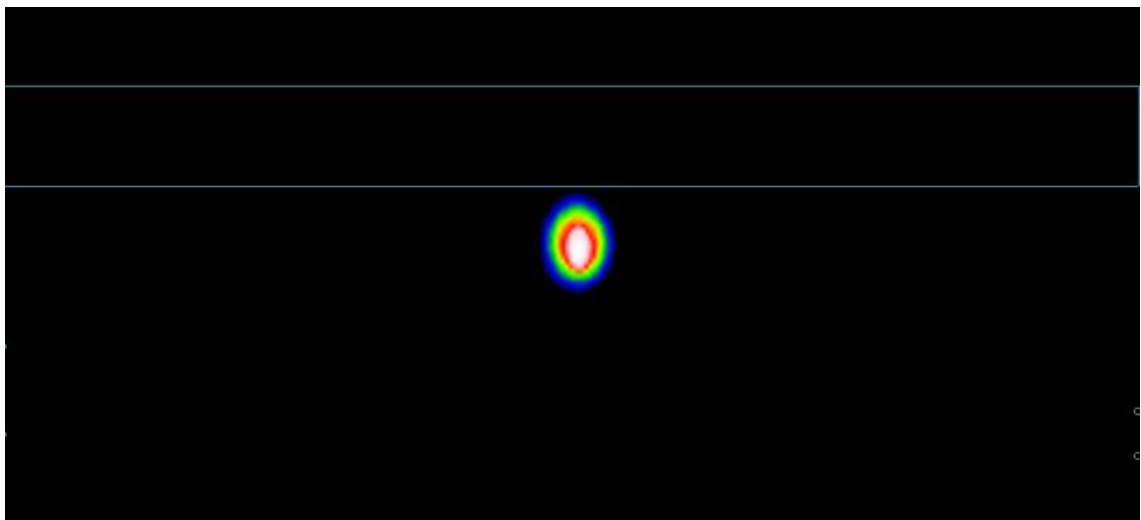


Figure 5.7: A CCD image containing a 20×20 pixel spot illuminating the device with 100 picowatts of power.

The optical setup described above results in an incident beam intensity of 100 pW at 532nm and a total area of 400 pixels. This generates an incident flux of 0.25pW per pixel. Given an integration time of 1 second, 0.25J of energy was incident on each pixel, which equates to 671×10^3 photons of wavelength 532nm incident on each pixel.

Assuming the detector has a QE of 0.9 (see Table 5.6), the incident photons would generate ~ 604545 electrons per pixel. Using the ADU resolution of $24.66 \text{ e}^-/\text{ADU}$, a CCD image of the incident beam would have a resultant value of 24515 ADU. It is important to note that this illumination would cause the ADC to saturate (as per the calculation above).

Figure 5.8 shows the pixel ADC values extracted from the CCD image shown in Figure 5.7. The central pixel has a digital value of 15403 ADU. This is a factor of 0.628 smaller than the theoretical value of 24515 ADU, indicating that the system was performing appropriately.

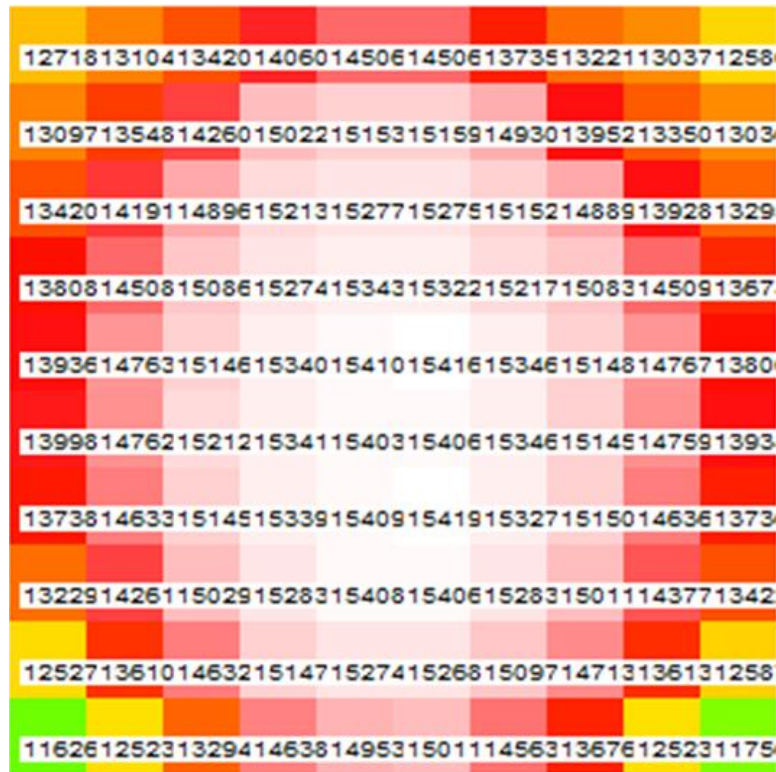


Figure 5.8: A zoomed-in image of the centre of the beam incident on the detector (see Figure 5.7). The image shows the ADU values of 10x10 pixels at the centre of the beam.

5.3 SYSTEM PERFORMANCE VERIFICATION

So far, this chapter has presented the throughput measurements of each subsystem of the Raman instruments that were described in Chapter 3, as an assessment of instrument performance. The sections below provide details on two additional studies that were performed in order to assess the instrument's performance. The first study uses the RLS prototype instrument to detect and characterise organic molecules in a host material, through minor shifts in the Raman bands produced by the molecules. The study provides a method of assessing the limits of the instruments spectral range.

The second study presents spectra acquired from sulphur (at stand-off distances) in comparison to spectra obtained by an in situ instrument. The SNR of the spectra will highlight the performance differences between the two systems, verifying the model presented in Chapter 3.

5.3.1 SPECTRAL RESOLUTION

Carotenoids are coloured organic compounds, often synthesised by extremophiles for UV radiation screening and DNA repair. Due to of their unequivocal biological origin many studies have concentrated on using Raman spectroscopy to detect and characterise carotenoid molecules produced by extant extremophiles (such as cyanobacteria), living in extreme cold or hypersaline environments, analogous to the Martian surface or subsurface (Wynn-Williams, 2000; Wang, Haskin, *et al.*, 2006; Jehlicka, Culka and Edwards, 2010). In addition, 514nm and 532nm excitation wavelengths coincide with energy of electronic transitions within carotenoid molecules resulting in the Resonance Raman effect (see Chapter 1, Section 1.3.1). This enhanced scattering effect increases the signal and allows for unambiguous detection of carotenoids in materials even at trace levels (Vítek, Osterrothová and Jehlička, 2009).

Carotenoids are complex molecules primarily composed of a conjugate C=C chain with pendant methyl groups. The molecule produces three main Raman bands: the first (ν_1) lies at a wavenumber shift of 1515cm^{-1} and is produced by the stretching of C=groups. The second band (ν_2) is located at 1157cm^{-1} and is a result of C-C stretching. The third band arises due to rocking of the CH_3 group and appears at 1008cm^{-1} (de Oliveira *et al.*,

2009). The position of the ν_1 and ν_2 bands are dependent on the number of conjugate double bonds. A longer conjugate chain will cause the ν_1 and ν_2 bands to shift to lower wavenumbers. As a result, different types of carotenoid materials can be identified and characterised by measuring the positions of one or more Raman bands (de Oliveira *et al.*, 2009; Jehlička and Oren, 2013).

However, the carotenoid band shifts are of the order of $\sim 3\text{cm}^{-1}$ (Culka *et al.*, 2014), therefore a Raman instrument must have a high enough spectral resolution to detect the shifts in order to identify the carotenoids.

In this study, a sample hosting several different carotenoid pigments is used to demonstrate the spectral performance of the RLS prototype instrument. The sample is a crystalline gypsum crust from a saltern pond near Eilat, Israel (see figure 5.9). Embedded in the gypsum are stratified cyanobacterial colonisations, known to produce a carotenoid known as β -carotene (Jehlicka, Culka and Edwards, 2010; Culka *et al.*, 2014). Since the discovery of evaporitic minerals, such as gypsum, on the Martian surface by the Spirit and Opportunity Rovers, samples such as these have become particularly relevant to the preparation for ExoMars and other astrobiological studies.

To assess the instrument performance in terms of spectral resolution, a robust calibration method was required to minimise the chance of bands moving due to detector or optical movement. In this study, calibration spectra of acetaminophen were obtained before and after sample rearrangement. In addition, the laser stability had to be considered since thermal fluctuations can cause wavelength shifts (on the scale of spectral acquisition times), which would appear as band shifts. The laser used in this study was the Excelsior DPSS laser (described in Chapter 3 Section 3.1.2). The laser was maintained at room temperature ($\sim 25^\circ\text{C}$) using a TEC. Finally, a minimised laser spot size (e.g. $50\mu\text{m}$ in diameter) gave the instrument a high spatial resolution, which is required to analyse the stratified β -carotene material. The RLS prototype was operated in Configuration 4 (see Figure 3.1), using the HoloPlex HPG-532 spectrograph, SXVR-H9 USB2 camera system (described in Section 3.1.5) cooled to $\sim 0^\circ\text{C}$. In that configuration, the instrument had a spectral resolution of $\sim 3\text{cm}^{-1}$.

Like many Raman studies, sample preparation was unnecessary as spectra were acquired from each layer at the sample surface. The sample, shown in Figure 5.9, comprised of 6 different layers in total, each differentiated by colour: red, purple, pink (a mixture of red and purple), orange, green and black. For each acquisition, the laser spot was focused onto the sample surface and at least 10 spectra were acquired from each layer. Integration times varied between 8-40s, depending on the fluorescence level and sample response.



Figure 5.9: A photograph of the Eilat sample, clearly showing the various pigments (colours) layered throughout the sample.

Figure 5.10 shows example spectra obtained from each layer of the Eilat sample. In each spectrum the ν_1 , ν_2 and ν_3 carotenoid bands are clearly visible, each with an SNR value above 500. In the red, pink and purple measurements, the positions of the three main bands are 1510 cm^{-1} (ν_1), 1154 cm^{-1} (ν_2) and 1012 cm^{-1} (ν_3). The carotenoid bands positions in the green and orange layers are 1516 cm^{-1} and 1515 cm^{-1} (ν_1), 1157 cm^{-1} (ν_2) and 1012 cm^{-1} (ν_3) respectively. There is a 5 cm^{-1} shift to a lower wavenumber of the ν_1 band and a shift of 3 cm^{-1} for the ν_2 band for the red, pink and purple layers, compared to the green and orange layers. A dotted line has been added to Figure 5.10 to show the ν_2 shift clearly. The position of the carotenoid bands in the black layer of the sample are 1509 cm^{-1} (ν_1), 1152 cm^{-1} (ν_2) and 1012 cm^{-1} (ν_3).

From these band positions, it is appropriate to infer that the carotenoids detected red, pink and purple layers of the Eilat sample have a large number of conjugate bonds compared to those detected in the green and orange sections of the sample.

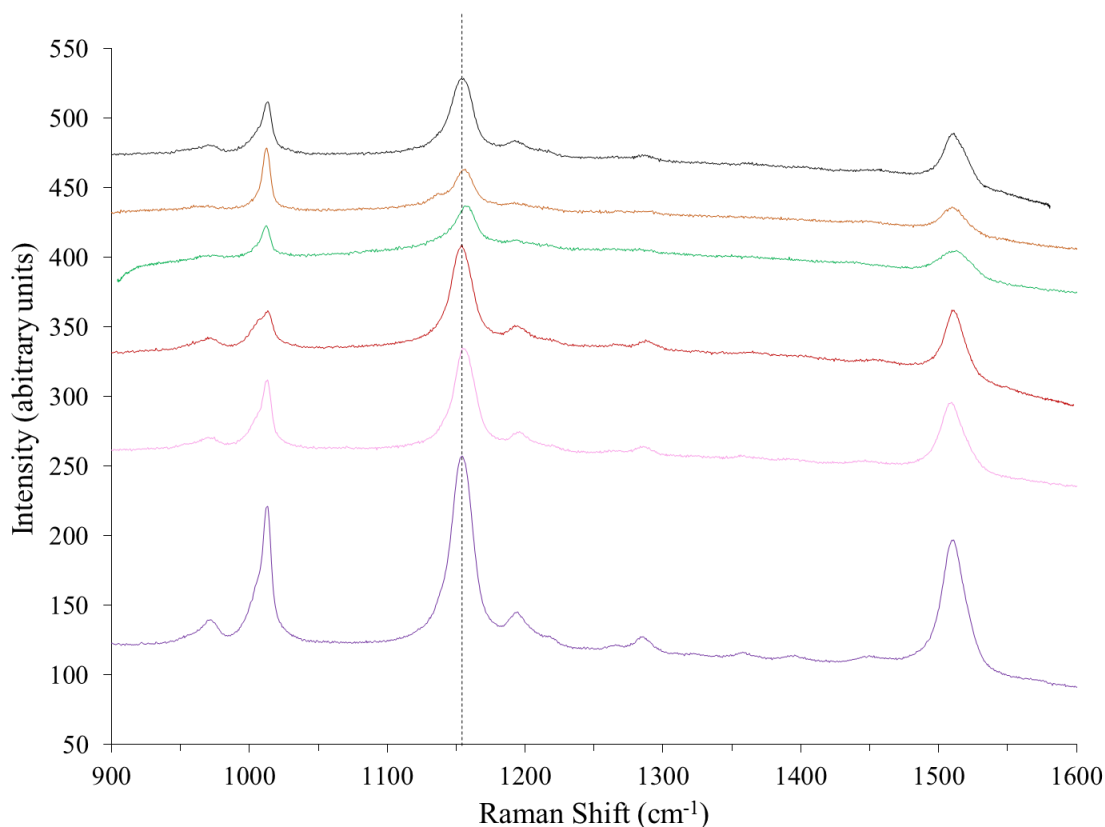


Figure 5.10: Spectra acquired from each layer of the Eilat sample.

To check that the band shifts were a result of molecular differences (and were not caused by calibration errors), each spectrum was self-calibrated (in addition to the original calibration), with self-consistent results. The stability of the laser was inferred from the lack of visible shifts observed in the ν_3 bands.

From these results it is evident that the instrument in this configuration is capable of resolving band shifts as small as $\sim 3\text{cm}^{-1}$, assuming the subsequent spectra obtained also had a high SNR.

5.3.1 STAND-OFF PERFORMANCE

NASA's Mars 2020 mission will deploy a stand-off Raman spectrometer on the surface of Mars (i.e. the SuperCam instrument). To fully understand the performance and

limitations of a stand-off Raman instrument it is important to understand the impact of hardware variations, operating modes and environmental conditions. Chapter 4 described (using a radiometric model) how different lasers, different detector operating modes and different levels of ambient light affect the performance of a Raman instrument. This section extends this work to consider the impact of working at extended working distances and explores the impact of using a gated detector, frame stacking and the use of an intensified detector. The results are then compared to spectra acquired using a standard long signal integration mode (i.e. an approach that already has higher TRL) to evaluate the instrument performance in each scenario.

The instrument used in this study is comparable to Configuration in 6 described in Chapter 3 (see Figure 3.1). Both systems include the Surelite I-10 Nd: YAG, the Mead ETX-125 Maksutov-Cassegrain telescope and the HoloPlex HPG-532. The instrument also incorporated the PI-Max4 Princeton camera system.

The study used sulphur as a standard sample because not only does it have a large Raman cross section (resulting in intense Raman bands), but it has been listed as a key target for future Venus missions since evidence of a sulphur cycle has been discovered on the planet (Wang, 2009).

The sample was unprepared and positioned at a distance of 3.3m from the telescope. Data were acquired in dark conditions, with the detector cooled to a temperature of -20°. Spectra were acquired using Princeton's LightField software.

Firstly, spectra were acquired using gated detector operation, synchronised to the pulsed laser output. The laser operated at a frequency of 6Hz, pulses were 8ns in duration and delivered at 35mJ/pulse to the sample. The camera integration time was reduced to 9ns and was synchronised to capture the laser pulses. A total of 400 frames were stacked to produce the spectrum in Figure 5.11(a). Spectrum (b) was obtained using identical acquisition parameters, however the gated PI-Max4 system was intensified (see Chapter 2, section 2.2.1). Only 300 frames were stacked to produce the spectrum. Spectrum (c) was obtained by using the detector in a standard 'signal integration mode' (i.e. the camera was not gated or intensified but the signal was integrated for 20 seconds before a single frame was read out from the device).

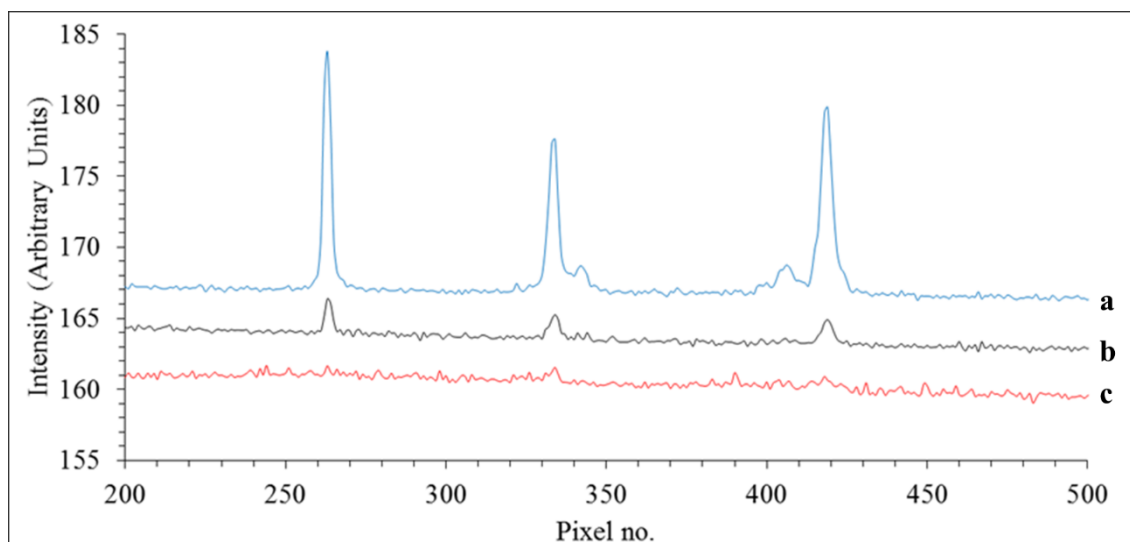


Figure 5.11: Spectra acquired using different operating modes at varying working distances. (a) a sulphur spectrum acquired from a sample at 3.3m away from the sample by stacking 400 frames and gating the detector. (b) a sulphur spectrum acquired at a working distance of 3.3m using a gated and intensified detector and by stacking 200 frames. (c) a sulphur spectrum acquired at a working distance of 3.3m using a non-gated non-intensified detector.

A total of 5 sulphur bands are visible in spectrum (a), at 262, 332, 340, 409, 418 pixels. However, in spectrum (b) only 4 sulphur bands are apparent, as the least intense band at pixel 409 is no longer visible. Only 2 sulphur bands are apparent in spectrum (c): one at pixel 332 and one at pixel 418.

The effects of stacking frames are discussed and modelled in Chapter 4. The studies presented in that chapter suggest that frame stacking can have an overall positive effect on the SNR ratio of a spectrum. This is clearly the case when considering spectra (a) and (b), which are composed of 400 and 200 frames, respectively. Despite the incorporation of an intensifier (the use of intensifiers is discussed in Chapter 2, section 2.2.5) in the case of spectrum (b), stacking frames resulted in a higher SNR for all Raman bands. For example, the SNR values for the band at 219cm^{-1} (the band visible in all spectra) for spectra (a) and (b) are 1732 and 1653 respectively.

In comparison to spectra (a) and (b), which were acquired with gated operation, spectrum (c) suggests that the instrument performance has diminished. Nonetheless, it is important to consider the SNR of the bands: the vibration mode at 219cm^{-1} still has an SNR value of 909, a sufficiently high value to identify a band. However, the lack of corroborative bands in spectrum (c) would make the mineral identification process ambiguous.

5.4 RADIATION DAMAGE CAMPAIGNS

Where appropriate the radiometric simulator (described in Chapter 4) can simulate radiation induced defects into the charge grid. Five types of trap are added to the charge grid at this stage: Silicon A, Silicon E, VV1, VV2 and unknown (the nature and cause of these defects is described in Chapter 2, Section 2.2.1.1). The total number of each trap type in a particular device is calculated based on the given type of detector (the amount of silicon subject to radiation) and the radiation dose it has received. The release and capture time constants for each type of trap are calculated using their specific energy levels, cross sections and the device operating temperature. These time constants are then used to calculate the probability of electrons becoming captured or released over a given time period (i.e. readout). Once the properties of each trap are calculated they are distributed randomly over the Charge Grid. Figure 5.12 shows a zoomed-in section of the Charge Grid, after the traps (orange flecks) have been distributed. The effects of the radiation damage become apparent during the simulated CCD readout process and in the final, digitised detector image.

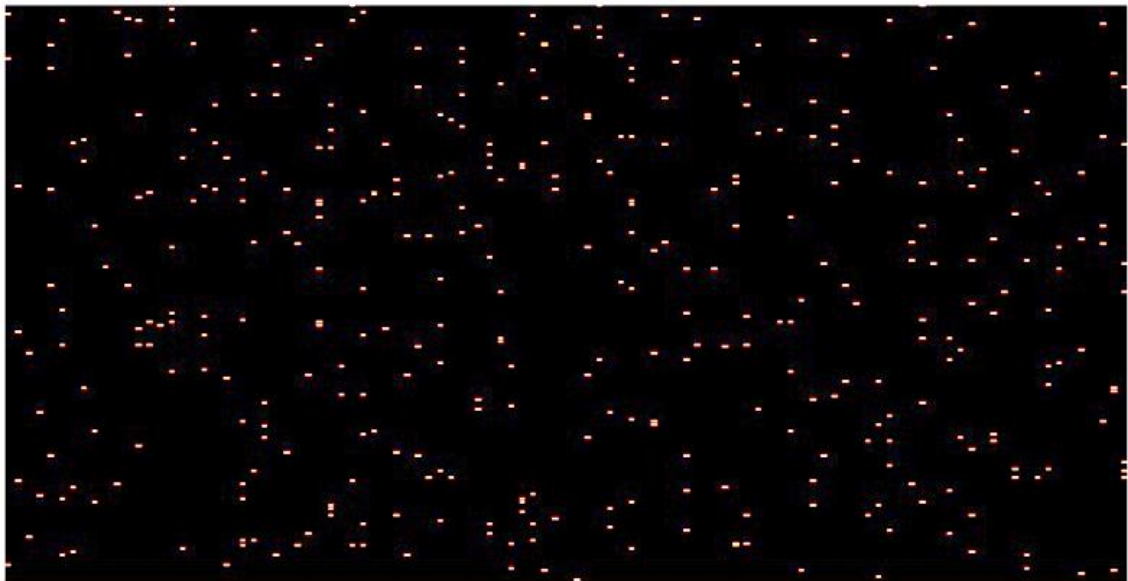


Figure 5.12: An image of the simulated charge grid showing the locations of randomly distributed charge traps (orange flecks).

Radiation traps impact on the charge transfer efficiency of a device, the effects of which can be observed in an acquired CCD image. The simulation can be used to demonstrate these effects by shifting a charge package (generated by a point source of light) through a radiation damaged region in a CCD and plotting the vertical charge intensity generated by the point source as a function of pixel number. Due to optical effects (discussed in

Section 5.2.2) a point source will initially exhibit a Gaussian profile on the detector, however the charge capture and release processes that occur will alter this Gaussian shape.

If the trap density in the region is sufficient then a significant amount of charge will be immediately captured (capture time constants are relatively small). If the device is operating at a warmer temperature then the release time constants will also be relatively short. Therefore, charge is likely to be released on the time scale of a row shift and consequently charge is not likely to be displaced out of its original pixel. In this case, the CCD image contains an unaltered Gaussian spot from a point source. An unaffected vertical cross section of it can be seen in Figure 5.13.

However, if the device is operating at a relatively low temperature (perhaps to reduce the level of dark current generated during operation), the release time constants will be larger. Charge is more likely to be released after a period of time longer than the time taken to shift a row. In this case, charge can be released back into a pixel after the bulk charge from the incident light has been shifted past. This effect is apparent in the vertical cross section acquired at lower temperatures (featured in Figure 5.13). For example, the left-hand side of the profile acquired at -40°C is steeper than that of the undamaged profile. This effect is caused by charge capture within the first few pixels that interact with the radiation damaged region, but since the operating temperature is relatively low, the charge is not released on the time scale of a row shift. It is, therefore, removed from the front of the profile. Similarly, because the release time constants are relatively long, the captured charge is more likely to be released once the integrated spot has been shifted through multiple rows, causing a tail of delayed charge release behind the profile. It is evident

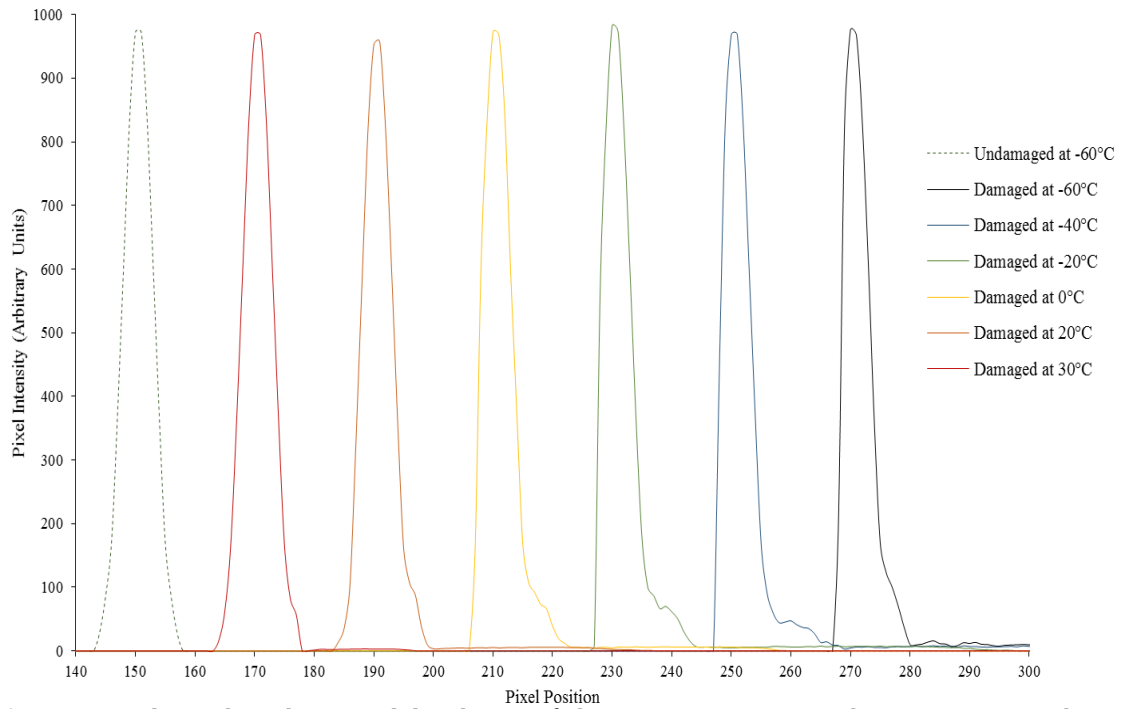


Figure 5.13: Plot to show the vertical distribution of charge in a CCD image. The image contains charge generated by a point source (which originally exhibits a Gaussian distribution due optical convolution effects).

from Figure 5.13 that the extent of the charge in the leading edge is redistributed is inversely proportional to the operating temperature of the device.

To verify the performance of the simulator, damaged devices have been incorporated into a bench-top stand-off system. Images are acquired using the damaged detectors and the impact on the spectrum is used to confirm the suitability of the modelled algorithms. This section provides details on the TID tests performed on a CCD230 in order to verify the parameters used in the simulation (described in the previous section). Two separate regions of the CCD230 device were damaged, one by a proton beam and the other by a gamma source, leaving a central section of the device undamaged. This approach provides a means of direct comparison between damaged and un-damaged performance for a given device type. The two radiation damage campaigns are described below. The total dosages used are comparable to those received by flight devices.

5.3.1 PROTON IRRADIATION- SCANDITRONIX MC-40 CYCLOTRON

The Scanditronix MC-40 cyclotron operated by Alta Cyclotron Service Ltd., a business associated with the University of Birmingham, can deliver protons with energies between

7 and 40MeV in circular beam profiles of 2cm, 4.3cm or 5cm diameter to targets mounted in air or vacuum.

Figure 5.14 shows a schematic of the device, highlighting the specific areas on the device which were irradiated with protons. For this campaign, fluences at the CCD were 2×10^9 (low), 5×10^9 (medium) and 5×10^{10} (high) protons per cm^2 with a proton energy of 10MeV. The CCD230 package incorporates a temporary glass window, which was not removed during the irradiation, in order to deliver 10MeV protons to the surface of the CCD, since protons with energy 17.6MeV were delivered to the window surface. Figure 5.19 shows a diagram of the device, indicating the thickness of the shield (preventing the irradiation of the entire device) and the glass window. Figure 5.15, shows the dimensions of the damaged areas and the allocated dosage.

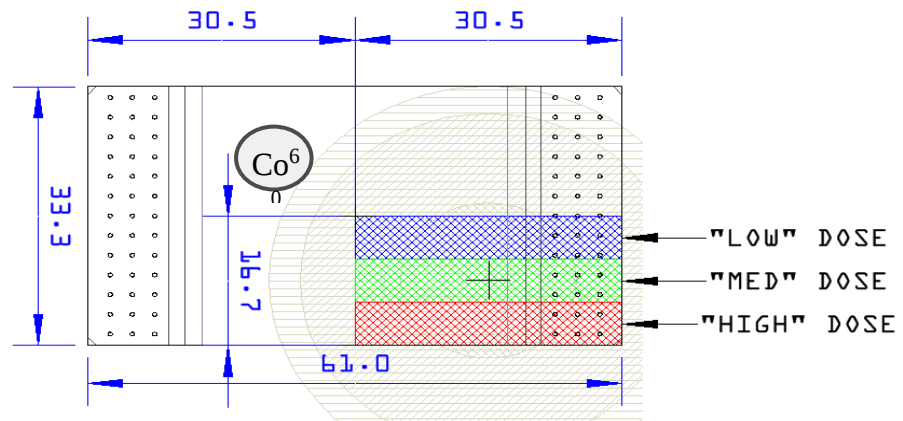


Figure 5.14: A schematic showing the size and dosage received of each region on the CCD230 device. Co^{60} indicates the region irradiated with gamma radiation.

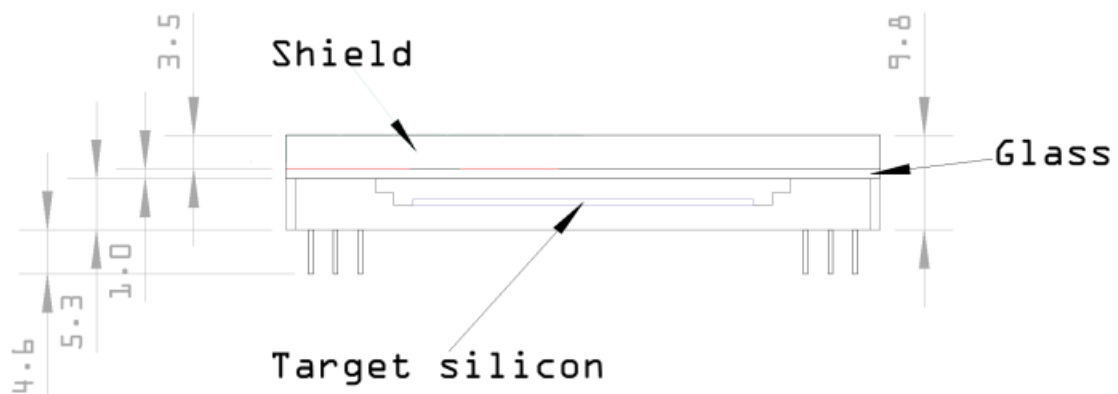


Figure 5.15: A schematic of the CCD230 device, illustrating the dimensions of the various components within the package.

Figure 5.16 shows two images acquired with the CCD230 after the proton damage test was completed. The varying levels of damage are indicated above the image. Clearly

there is an increase in dark current and bright pixels, but Raman spectra can still be recovered. It was verified that after cooling to -10°C , the dynamic range achieved was sufficient to meet the primary scientific requirements for the mission (see Ingley et al., 2014 for the dynamic range required for typical dynamic range requirements).

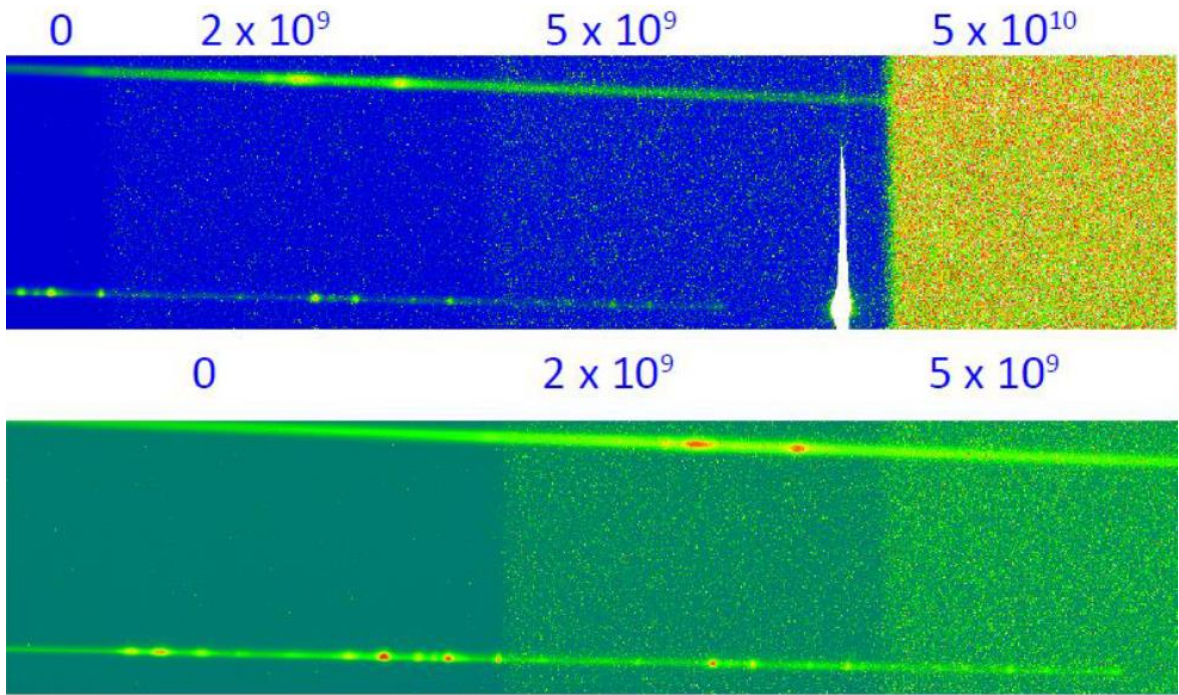


Figure 5.16: Two images acquired using the CCD230 subsequent to the proton damage campaign.

5.3.1 GAMMA IRRADIATION- ESTEC Co^{60} FACILITY

The Co^{60} facility located at ESTEC, was used to deliver gamma radiation to the CCD230 device. The Co^{60} source has a half-life of 5.25 years, and decays by beta emission to Ni^{60} . The activated Ni nucleus emits two photons with energies of 1.173MeV and 1.332 MeV. A diagram of the radiation chamber of the facility can be seen in Figure 5.17.

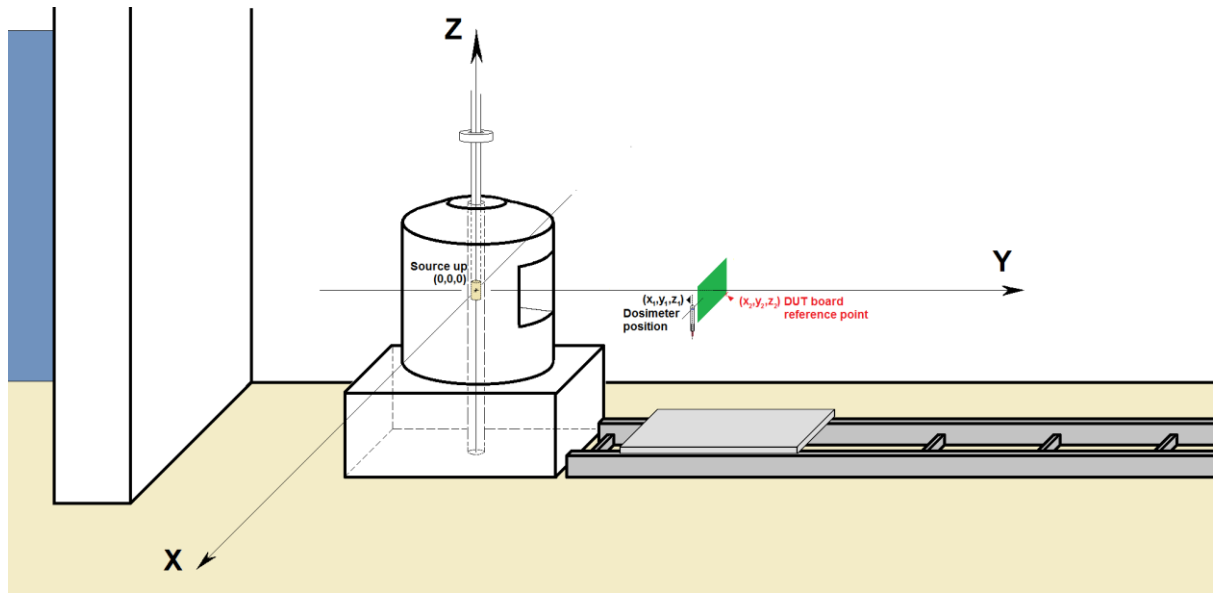


Figure 5.17: A diagram of the Co60 chamber at ESTEC. The detector and headboard were set-up on the grey, moveable slab visible in the diagram.

The CCD230 device (and its associated electronics) were located in the chamber such that they received a TID of 123Gy (12.3Krad) over 2 days. The experimental set up is illustrated in Figure 5.17. To prevent the entire device from receiving the full dose, the setup incorporated (up to) 10cm of lead shielding in order to impede >99% of the radiation. This can be seen in Figure 5.18. The unshielded region is highlighted in Figure 5.14 by the Co60 marker. The extent of the shielding can be seen in Figure 5.18, as well as the dosimeter, which was positioned directly above the device.

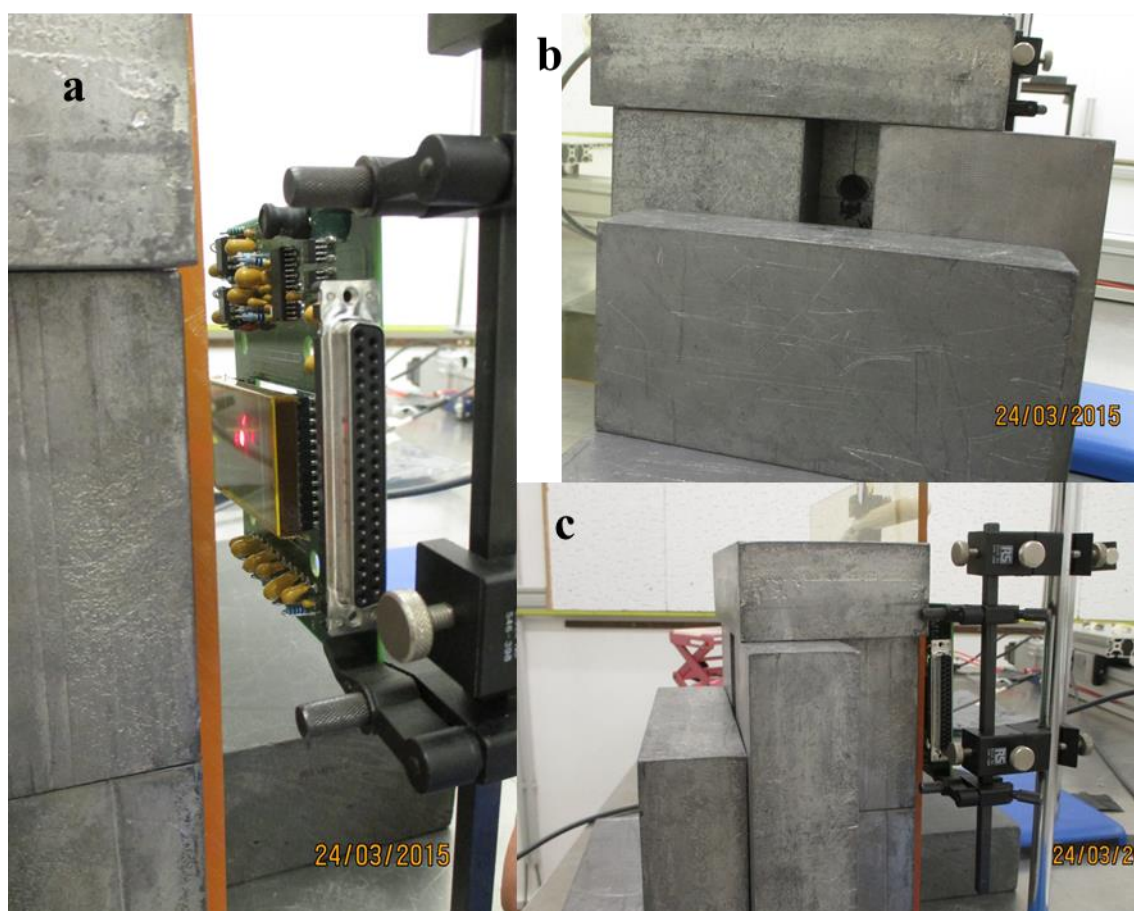


Figure 5.18: Photographs of the radiation campaign set up that took place at the Co60 facility at ESTEC, NL. (a) Shows the detector situated behind the shielding. The photo also shows a laser spot indicating the region damaged by the Co60 source. Photographs (b) and (c) show the extent for the LEAD shielding.

5.5 SUMMARY

This chapter describes the development of software to control laboratory and field instrumentation to enable end to end testing and the collection of verification data. The panel based system provides a method of controlling and optimising CCD image acquisition, Raman spectral extraction, motorised instrument movement and system thermal stability.

This chapter also presents the measured throughput of each component in the RLS prototype as well as the stand-off Raman instrument developed for this PhD. The measured throughput of each component and subsystem is then compared with theoretical throughput measurements produced by the radiometric model presented in Chapter 3, Section 3.2.

In addition to throughput modelling and measurements, the chapter describes two Raman spectroscopy studies that were performed to assess system to assess the instrument's performance. The first study uses the RLS prototype instrument to detect and characterise beta-carotene molecules (produced by extremophile organisms) in a terrestrial halite matrix. The analysis was used to verify that the spectral resolution of the RLS prototype (in a given configuration) was $\sim 3\text{cm}^{-1}$ and anticipate the performance of the RLS instrument on board ESA's ExoMars mission.

The second study presents spectra acquired using the stand-off instrument described in Chapter 2, Section 2.1. The spectra were acquired from a sulphur sample at a stand-off distance of 3m and compared to spectra obtained by an in situ instrument to verify the effects of working distance and operating modes presented in Chapter 3.

Finally, this chapter modelled effects of radiation damage on CCD detectors using the radiometric model described in 3 and the Monte Carlo simulation presented in discusses the instrument operations that can be implemented to reduce its impact. The section then describes two radiation damage campaigns that were completed at ESTEC and the Scanditronix MC-40 cyclotron in order to verify the effect of radiation damage on the CCD detectors.

6 ANALYSIS OF MISSION RELEVANT SAMPLES USING FLIGHT REPRESENTATIVE INSTRUMENTATION

Throughout the instrument development process, it is important to assess the performance and limitations of an instrument when faced with realistic environmental challenges and real-world/natural samples. This chapter presents two instrument performance studies completed in preparation for future planetary missions. The first study concerns the Compact Integrated Raman Spectrometer (CIRS) instrument developed by Washington University, USA, the NASA Jet Propulsion Laboratory and the University of Leicester. CIRS was first designed for NASA's Mars 2020 mission but is now being considered for future Venus and outer solar system moon missions. An instrument prototype (TRL 6) was used to obtain spectra from a range of mission relevant minerals in order to assess performance and mineral detection limits.

The second study was completed in preparation for ESA's ExoMars mission, which is due to launch in 2020. The investigation utilises the Raman Laser Spectrometer (RLS) simulator and the Sample Preparation and Distribution System (SPDS) emulator to replicate the ExoMars mission sample analysis sequence. A comprehensive range of mineral studies has been performed with the system (Foucher *et al.*, 2013; Lopez-Reyes *et al.*, 2014; Bost *et al.*, 2015), but here the focus is on analysis of spectra obtained from an analogue of a carbon bearing meteorite sample. The specific aims of the study were to measure the spectral band characteristics of thermally altered carbon to see if the ExoMars instrument will be able to discern it from non-thermally altered material.

6.1 ANALYSIS OF STANDARD SAMPLES USING THE MARS MICROBEAM RAMAN SPECTROMETER

6.1.1 STUDY MOTIVATION

Very little is known about the surface geology and mineralogy of Venus due to the planet's dense atmosphere, high pressure and extreme temperatures. The history of Venus exploration and the key findings from past exploration missions are described in Chapter 1, along with a description of the gaps in our knowledge of the planet and the key scientific questions that future missions will aim to answer. In 2011, the Decadal Survey for Planetary exploration listed Venus as a priority target for future NASA lander missions in the decade 2013-2022 (Committee on the Planetary Science. 2011), stating several Venus in situ missions as candidates for the New Frontiers mission category.

Following this, the NASA Science Definition Team for the Venera-D mission (due to launch in 2022) has identified Raman spectroscopy as a key analytical tool for the future in situ exploration of Venus and describes the technique as desirable for assessing the mineralogy on the surface of the planet (Senske *et al.*, 2017). The Venera-D science goals include the detection and characterisation of igneous, hydrothermal and sedimentary rocks at the surface of the planet. In the past, many studies have used Raman spectroscopy to not only identify carbonates but also to investigate the cation ratios (Herman *et al.*, 1987). Work completed by Wang *et al.* (2004) showed that Raman spectroscopy is ideal for observing Mg, Ca and Fe sulphates as well as their phase transitions. Wang *et al.* (2004) also showed that the presence and abundance of igneous minerals such as olivine's, pyroxenes, feldspars, Fe-Ti-Cr oxides and phosphates can be detected using Raman spectroscopy.

Raman spectroscopy is also suitable for analysing both solid and gaseous material making it an ideal tool for analysing the Venusian cloud layers (Senske *et al.*, 2017). Past missions have discovered evidence of surface and atmospheric interactions with the planet through a sulphur cycle (Crisp *et al.* 2002). Studies have shown that techniques such as Raman spectroscopy are sensitive to SO_3 , HSO_4 , $(\text{SO}_4)_2$, and $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ complexes in igneous rock (Wang. 2009).

The final Venus mission objective highlighted by the Venera-D Science Definition team was the search for evidence of water and organic material. Berenblut et al. (1971) showed that Raman spectroscopy is highly sensitive to calcium sulphate minerals at varying levels of hydration (gypsum and anhydrite for example) and many studies have shown that these minerals could be used to identify the presence of water on a planetary surface (Liu, Wang and Freeman, 2009). The Raman technique has also been shown to be highly sensitive to organic material, especially when utilising the resonance Raman technique (see Chapter 1, Section 1.3.1). Indeed, many studies have shown that trace amounts of organic molecules such as Beta carotene are detectable with mineral matrices when using Raman spectroscopy (Marshall *et al.*, 2007; Vitek, Osterrothová and Jehlička, 2009; Vandenabeele *et al.*, 2012).

Additional advantages of utilising Raman spectroscopy for the exploration of Venus include the lack of sample preparation requirements and the ability to use the technique through a window. Data acquisition is also fast and non-destructive, meaning that an instrument can operate and perform an extensive analysis on the surface of the planet, even when limited to a short amount of time.

In preparation for future Venus missions such as Venera-D, the Jet Propulsion Laboratory and Washington University (in collaboration with the University of Leicester) have developed the Compact Integrated Raman Spectrometer (CIRS). The instrument is based on the Mars Microbeam Raman Spectrometer, a system developed originally for NASA's Mars Science Laboratory (MSL) mission (see Chapter 1, Section 1.3.4). Even though MMRS was unsuccessful in the instrument selection process for MSL, the system was listed as 'Category 1' (Sharma and Wang, 2007) and recognised to be a highly capable, analytical instrument. Taking benefit from the strong heritage and efficient design of the MMRS instrument, the CIRS instrument was developed rapidly and reached a TRL of 6 in 2016, providing future planetary missions (to destinations such as Venus) with a miniaturised, robust and highly efficient Raman spectrometer (Wang *et al.*, 2016). In addition to on-going field test campaigns in the Atacama Desert, the CIRS instrument is undergoing a set of laboratory based performance tests using mineralogical samples that are representative of those found on planetary surfaces in order to fully assess the capabilities of the system. Section 6.1.2 of this chapter describe the CIRS instrument and the selection of samples used to assess the instrument performance. The following section

also presents spectra acquired using the CIRS instrument in conjunction with the software developed for the CIRS programme (see Chapter, Section 5.1).

6.1.2 INSTRUMENT DESCRIPTION

The following section gives an in-depth description of the CIRS instrument (as described in Wang et al. 2016; Wang et al. 2003; Lambert J. L. et al. 2014 and Wang. et al. 2014). Figure 6.1 shows the internal structure of the CIRS system. The instrument utilises a Diode Pumped Solid State (DPSS) laser that produces a stabilised continuous wave emission at 532nm, with a power range of 0.5-50mW. The beam is focused through the instrument aperture onto the surface of the sample via a combination of mirrors and lenses. The focused laser beam is 35.7 μ m in diameter allowing for fine scale analysis of materials. The instrument also has a large depth of focus making the instrument tolerant to rough sample surfaces. The laser is also focused at a sufficiently large distance that it allows the instrument to operate through a fused silica or sapphire window, making it suitable for deployment on a Venus lander.

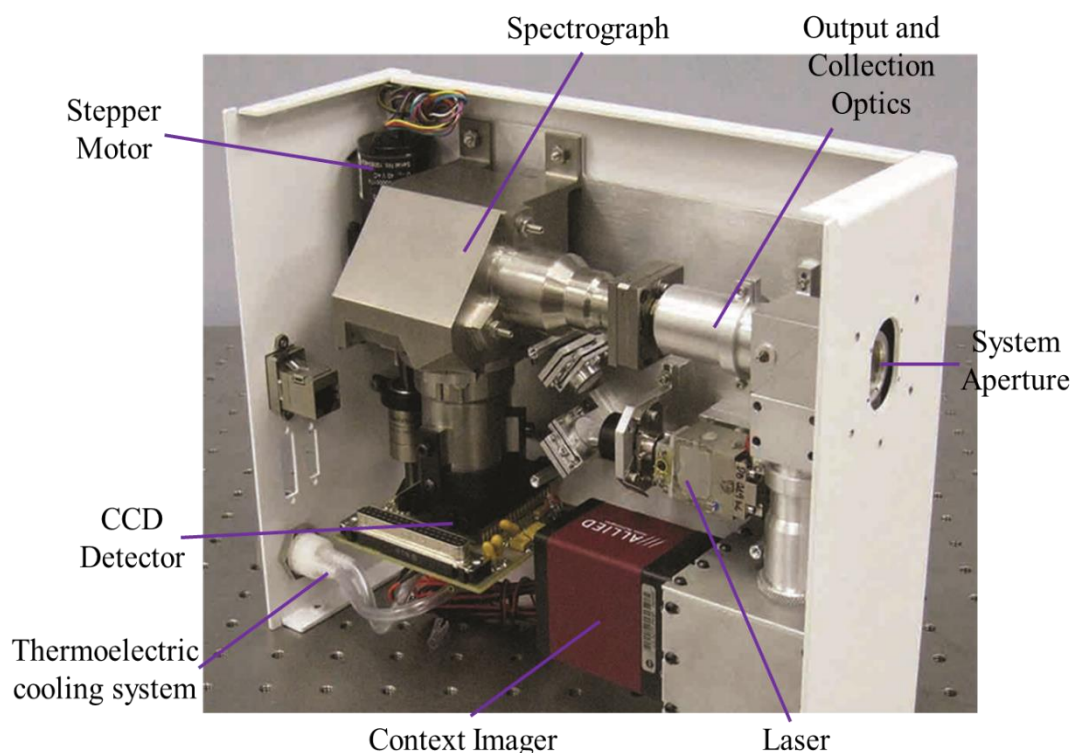


Figure 6.1: The Compact Integrated Raman Spectrometer developed by JPL and Washington University.

The spectrometer provides the system with a wide spectral range of 183cm^{-1} - 4432cm^{-1} and achieves a resolution of 9cm^{-1} , allowing for the detection of a broad range of molecular species.

The detector utilised by the system was provided by the University of Leicester and incorporates an inverted mode version of the CCD47-20 device, a frame transfer CCD manufactured by e2v technologies (see Chapter 2, Section 2.2.7). The device features 1024×1024 , $13\mu\text{m}$ pixels, each with a FWC of $\sim 100,000$ electrons. The quantum efficiency of the detector is $> 90\%$ within the spectral range of the instrument, and its associated FPGA based control and acquisition system is configured for an optimum dynamic range in excess of 10000:1 for a single spectrum. At this sensitivity level, the instrument is capable of acquiring spectra in 1-60s. The detector is cooled by an integrated thermoelectric cooler and water circulation system (shown in Figure 6.1).

The whole spectrometer is mounted to a stepper motor, which enables the instrument to scan across sample surfaces (collecting up to 100 spectra in less than 1 hour) or move between sample targets on a micron scale. To enhance the overall capability of the instrument, the system contains a context imager that provides geological context (it shares an optical path with the laser, resulting in a microscopic image of the area from which spectra is acquired).

6.1.3 SAMPLE DESCRIPTIONS

Three standard samples were used to assess the performance of the CIRS instrument: cyclohexane, gypsum and calcite. Cyclohexane is a cycloalkane chemical with the molecular formula C_6H_{12} . It is frequently used as a calibration sample as it provides many distinct and unambiguous bands, spanning a large spectral range (100 - 4000cm^{-1}). Gypsum is a hydrated calcium sulphate mineral, with the chemical formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In 2006 sulphate evaporates such as gypsum were identified on the surface of Mars, making the mineral an ideal standard sample for assessing the performance of Raman instrumentation for Mars exploration (Wang, Haskin, *et al.*, 2006). Finally calcite (CaCO_3) is a calcium carbonate mineral. Calcite was used as a standard sample in this study as it has been highlighted as a key biological target for future astrobiology studies

due to its association with extremophile habitats and preservation (Jorge Villar and Edwards, 2005).

6.1.4 METHODOLOGY

To assess the performance of the CIRS instrument on natural mineralogical samples, a number of spectra were acquired from each of the materials listed in Section 6.2.3. This was achieved using the Instrument Control Environment (ICE) described in Chapter 5, Section 5.1. A screenshot of the ICE software incorporating a spectrum acquired by the CIRS instrument is shown in Figure 6.2. For each acquisition, the laser power and integration times were optimised accounting for the strength of the Raman and fluorescence background signal. The average laser power used was 35mW while the integration times ranged from 1-60 seconds.

The data were extracted from the acquired CCD images (using the ICE software) by summing the image pixels containing spectral data. Pixel regions were minimised by fitting appropriate ROIs to the spectral emission in order to reduce noise (see Chapter 4, Section 4.2). The system was calibrated frequently throughout the experimental programme using cyclohexane.

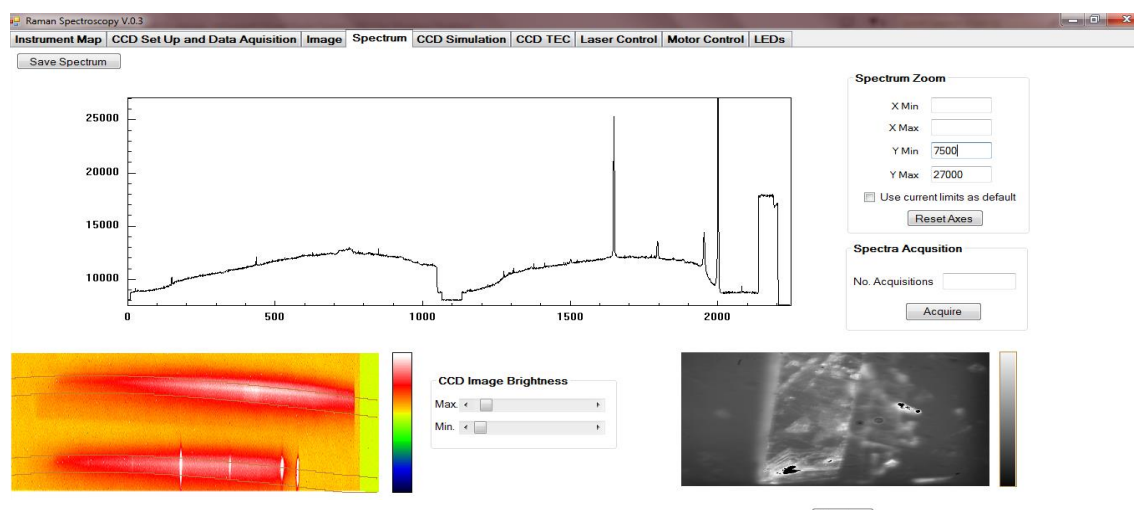


Figure 6.2: A screenshot of the Instrument Control Environment software used to control the CIRS instrument. The panel contains a CCD image and spectrum acquired by the spectrometer and a context image showing a magnified image of the sample.

6.1.5 RESULTS

Figure 6.3 shows a spectrum acquired from the cyclohexane sample. The spectrum shows strong features at 384.1 cm^{-1} , 426.4 cm^{-1} , 801.3 cm^{-1} , 1028.3 cm^{-1} , 1157.6 cm^{-1} , 1266.4 cm^{-1} and 1444.4 cm^{-1} . The spectrum indicates that the CIRS instrument demonstrates excellent performance over the full spectral wavelength range. The discernibility of the bands at 1157.6 cm^{-1} , 1266.4 cm^{-1} and 1444.4 cm^{-1} also show the instrument is operating with a spectral resolution better than $\sim 9\text{ cm}^{-1}$

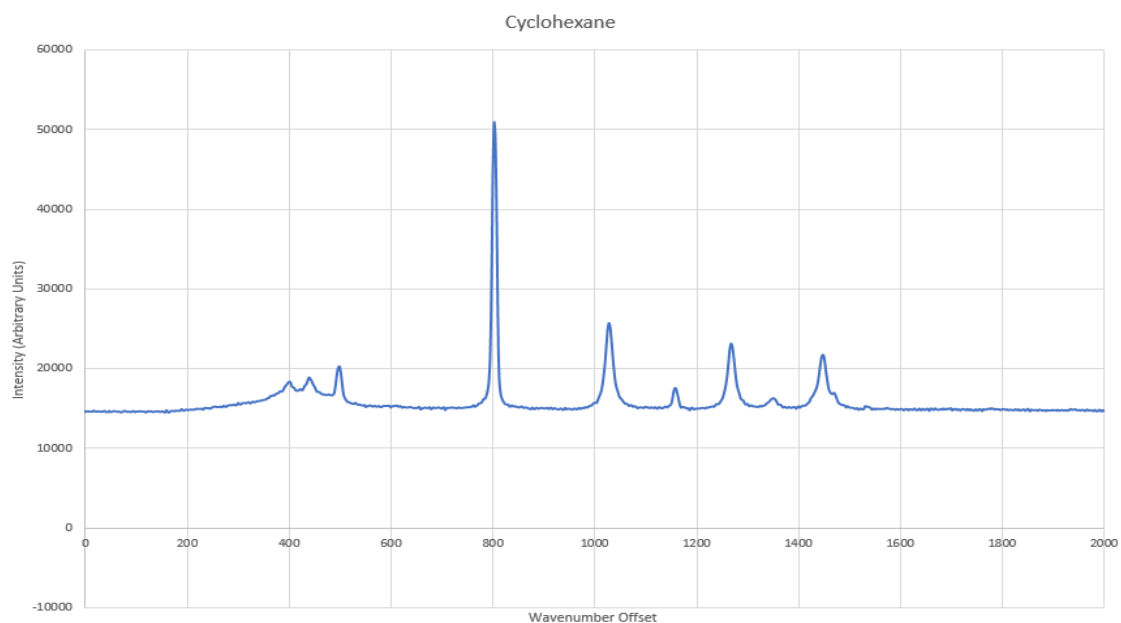


Figure 6.3: A spectrum obtained from cyclohexane using the CIRS instrument

Figure 6.4 shows the spectrum acquired from the calcite sample. The spectrum contains four strong signature bands at 149 cm^{-1} , 277 cm^{-1} , 704 cm^{-1} and 1082 cm^{-1} . The spectrum also indicates a low level of background noise.

Finally, Figure 6.5 shows a spectrum acquired from the gypsum sample using the CIRS instrument. The spectrum reveals five strong bands located at 1139 cm^{-1} , 1008 cm^{-1} , 619 cm^{-1} , 492 cm^{-1} , 413 cm^{-1} , 209 cm^{-1} , 179 cm^{-1} and 131 cm^{-1} . The spectrum also shows a low level of fluorescence in addition to low noise levels.

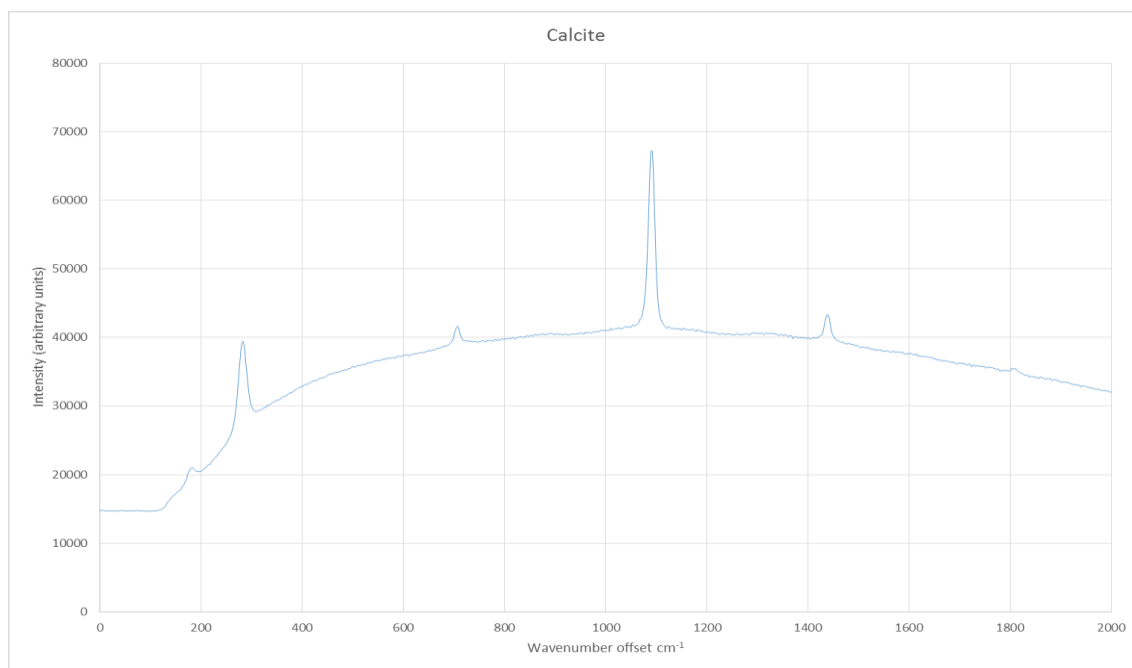


Figure 6.4: A Raman spectrum of calcite

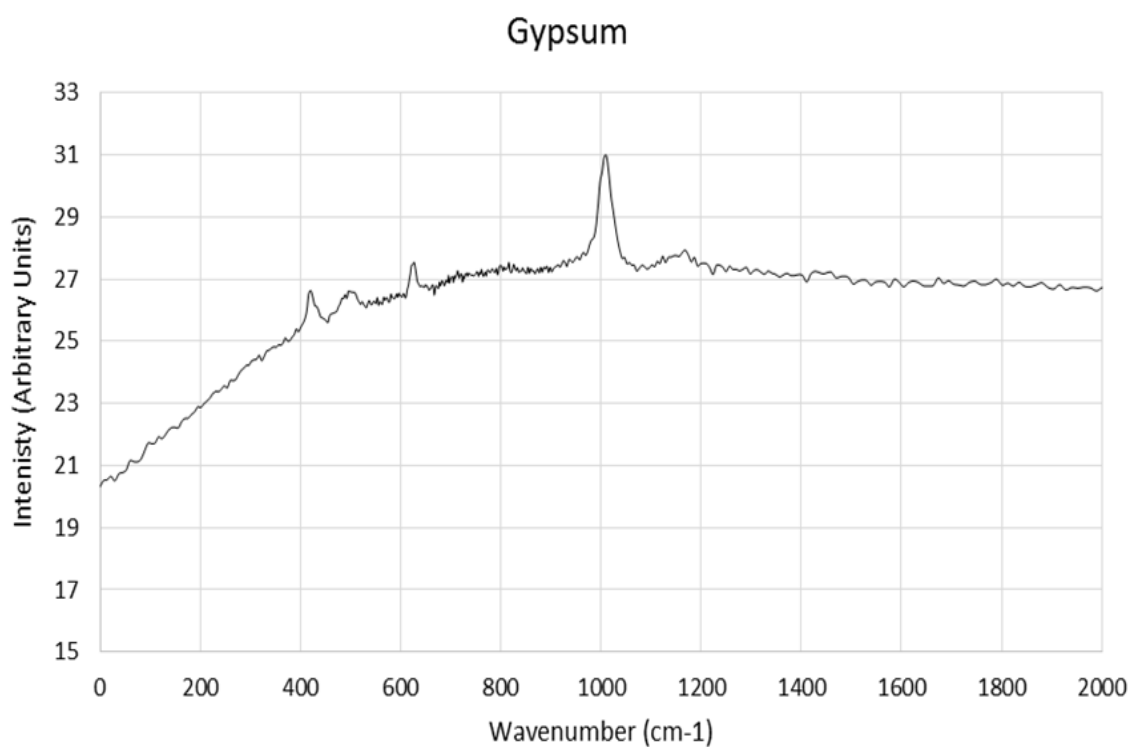


Figure 6.5: A Raman spectrum of gypsum obtain suing the CIRS instrument

6.2 ANALYSIS OF NAKHLITE METEORITE ANALOGUE USING THE RAMAN LASER SPECTROMETER SIMULATOR

6.2.1 STUDY MOTIVATION

Between the design and development stages and final deployment in space, it is vital to gain a realistic and detailed insight into how an instrument will perform once it has reached its destination. To assess the capability of a proposed instrument design (for instance, while it is still in its early stages of development) a range of laboratory based analogue studies are usually carried out (Olson and Craig, 2011) and, in some cases, full mission field campaigns (Chapter 7 discusses the importance of analogue missions and describes two campaigns undertaken for this purpose during the work).

Analogue studies often utilise a specific instrument configuration (usually comparable to an instrument flight design) to assess the sensitivity limits for particular types of material. These materials are often terrestrial in origin but scientifically comparable to target samples specified by mission objectives (i.e. chemicals/molecules that relate to the key mission science questions). For example, one of the major objectives of ESA's ExoMars mission (described in Chapter 1.1.2) is to search for evidence of past or present life on Mars (F. Rull *et al.*, 2011). Therefore, in preparation for the mission, many analogue studies have investigated the detectability of appropriate minerals and biomarkers (molecules uniquely derived from living organisms) and mineral/biomarker combinations (Edwards *et al.*, 2014). For example, a study by Vandenabeele *et al.* (2011) evaluated the detection limits of biomarkers (such as β -carotene) in solid matrices (for example, halite) using a portable Raman instrument. The study focuses on how the detection limit is affected by not only the concentration of the target material but also by the design of the Raman instrument. Moody *et al.* (2005) studied the molecular signatures produced by Antarctic extremophiles with the aim of developing a Raman database of biogenic modifications of geological structures. Further to this, Edwards *et al.* (2012) analysed a selection of analogue samples that have mineralogical and biogeological importance to the ExoMars mission. These include carbonaceous material, calcium carbonates, carotenoids and haematite.

However, these molecules are often complex and degrade under extreme environmental conditions, eventually forming carbon. Hydrocarbons (for example, either abiotic or biotic in origin) can be altered by thermal geological processes. These processes create order in the hydrocarbon material and strip them of the hydrogen atoms, forming large scale aromatic carbon structures, tending towards graphite. Carbonaceous material undergoing these processes is often referred to as reduced carbon and is the most likely product of biological processes to be encountered by analytical instruments (i.e. rather than complex hydrocarbons).

Although reduced carbon has not yet been detected on Mars, its presence on the surface is expected as a result of volcanic rock erosion and past meteor bombardment (McKay *et al.*, 2011). In 2011, evidence of reduced carbon was detected in carbonaceous Martian meteorites (McKay *et al.*, 2011). Since then, reduced carbon has become a high priority target (Hutchinson *et al.*, 2014) and several studies have focused on the suitability of portable Raman spectrometers for detecting and characterising reduced carbon (Pasteris and Wopenka, 2003; L. V. Harris *et al.*, 2015). For example, one investigation conducted by Parnell *et al.* (2014) focused on the analysis of a terrestrial analogue of the Nakhla meteorite using flight representative Raman instrumentation.

The presence of reduced carbon in a sample can be inferred from the identification of Raman bands, known as D and G bands, at $\sim 1350\text{cm}^{-1}$ and 1580cm^{-1} to 1600cm^{-1} respectively. The D band arises from the breathing mode of sp^3 bonded carbon atoms in an aromatic ring. This band is absent in completely disordered carbon or graphite. The G band results from the stretching of two sp^2 bonded carbon atoms. Since these bands arise from the macrostructure of carbon atoms, their presence and the characteristics of the G band in particular can be used to infer the geological history of the material.

Although several carbon studies have been pursued in the past few years, the work is incomplete and it is important to continue to explore the specific limits of flight instrumentation in order to fully assess its expected impact during mission operations. During this investigation, a carbonaceous terrestrial analogue of the Nakhla meteorite was analysed using the RLS scientific simulator with the aim to demonstrate both detection sensitivity to reduced carbon and a band characterisation capabilities that is sufficient to infer the thermal history of the material.

6.2.2 SAMPLE DESCRIPTION

Figure 6.6 shows the meteorite analogue sample used for this study. The sample originated from an ancient pillow lava flow (Sharpe, 1970) in a region now known as Helen's Bay, County Down in Northern Ireland. The area includes black (organic carbon-rich) shales and sandstones, as well as carbon bearing basalt within the pillow lava.



Figure 6.6: A photograph of the Nakhlite meteorite analogue sample from Helen's Bay in Northern Ireland. The photograph clearly shows the impact crater in the centre of the sample. The white veinlets are also visible running through and over the surface of the bulk material.

The Helen's Bay sample was chosen as an analogue to the Nakhla meteorite due to the embedded carbonaceous material seen within the bulk material (similar to those seen in the meteorite when studied by Steele *et al.* (2012)). However, it is thought that the carbon in the Helen's Bay sample originates from the thermal alteration of shales to form hydrocarbons, whereas carbon observed in meteoritic carbon is likely to be magmatic in origin. Carbon is also present in the millimetre-scale veinlets of quartz and carbon that run through and over the surface of the bulk material (clearly apparent in Figure 6.6). The veinlets result from hydrothermal movement of minerals to fill fractures in the bulk material.

To simulate further thermal stress, the sample was shocked using a two-stage light gas gun developed by the University of Kent. The gun is capable of firing millimetre sized projectiles at speeds of 1-5.7 kms^{-1} using pressured gas (hydrogen, nitrogen and Helium) (Burchell *et al.*, 1999). The impact crater can clearly be seen at the centre of the sample in Figure 6.6.

6.2.3 INSTRUMENT DESCRIPTION

Sample characterisation was performed by two different Raman spectrometers. The first was the RLS simulator located at the Centro de Astrobiología in Spain. The instrument was developed in order to simulate complex and autonomous RLS and SPDS-like analysis and operations. The flight representative system also provides a platform for developing optimised operating modes for the RLS instrument in order to maximise scientific return (Lopez-Reyes *et al.*, 2013). The system includes a sample container attached to an X-Y stage (see Figure 6.7). Sample movement in the X-direction simulates the SPDS system (with 2.5 μ m resolution), while the addition of mobility in the Y direction allows for full sample mapping capability. For comparison, the Raman Laser Spectrometer on ExoMars will be integrated into the Rover's Analytical Drawer along with Ma_Miss and Micro-Omega (for a description of these instruments see Chapter 1, Section 1.1.2). These instruments are supplied with flattened, powdered sample material (via the SPDS). Samples are crushed to a grain size of 200–250 μ m to avoid sampling issues associated with the possible inhomogeneity of the sample surface (i.e. the coverage of the sampling process is limited so key features on the surface of the rock may be missed) and allow analysis of the sample interior. In coordination with the SPDS, the RLS instrument will analyse at least 20 random points on the crushed sample surface.

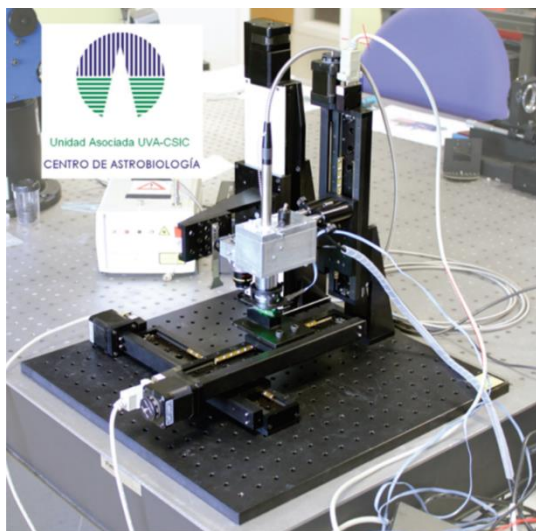


Figure 6.7: A photograph of the Raman Laser Spectrometer Simulator's optical head and XYZ translation system (taken from Lopez-Reyes *et al.* 2013).

The instrument also incorporates a Z translation system with an integrated optical head (also shown in Figure 6.7) to simulate (along with feedback algorithms) the RLS autofocus system. The optical head provides a 50 μ m laser spot (continuous) at the sample surface, which, with the 50mW, 532nm laser, matches the key RLS flight

instrument parameters (the RLS instrument will provide a laser spot size of 50 μ m and will irradiate the sample with 0.6-1.2kWcm⁻² at 532nm; see Rull et al. 2011).

Spectra were obtained using a Horiba Jobin Yvon iHR320 spectrometer (with a grating of 1200 g/mm) and a Spex ISA Spectrum One Nitrogen cooled CCD (Foucher *et al.*, 2013). In addition, the system incorporates an internal context imager is used to provide close up images of the sample. The camera system uses an identical optical path to the laser therefore the position of the laser beam can be seen in the images.

The RLS simulator uses a variety of algorithms to optimise the quality of the spectra in the shortest possible acquisition time (since there will be limited operating time while on the surface Mars). The algorithms optimise a number of parameters, including the focus position, the integration time and the number of acquisitions based on the signal-to-noise ratio achieved and variation with each parameter.

The second Raman instrument was a 632.8nm prototype bench top system composed of a Kaiser OSI MKII proper, a Spectrometer Kaiser OSI HoloSpec f/1.8i and a DV420A-OE-130, Andor CCD camera.

6.2.4 METHODOLOGY

In order to thoroughly investigate and characterise the various sources and forms of carbon present in the sample, three spatially separated areas of interest were identified on the surface: the crater, the white veinlets and the normal, unaltered material surrounding the other two areas (see Figure 6.6) The ejecta material generated from the impact process was also conserved for spectral analysis.

Using the RLS simulator system, spectra were acquired from multiple points along a surface transect of the Helen's Bay sample. The sample was placed on the XY translation stage and its position relative to the optical head was altered in 100 μ m steps (in the X direction). In total, 255 separate spectra were acquired from points along the transect line highlighted in Figure 6.8. At each and every sample point, the acquisition time and the

number of stacked spectra was optimised, with acquisition times ranging from 2.5 to 19 seconds and number of acquisitions ranging from 4 to 29.

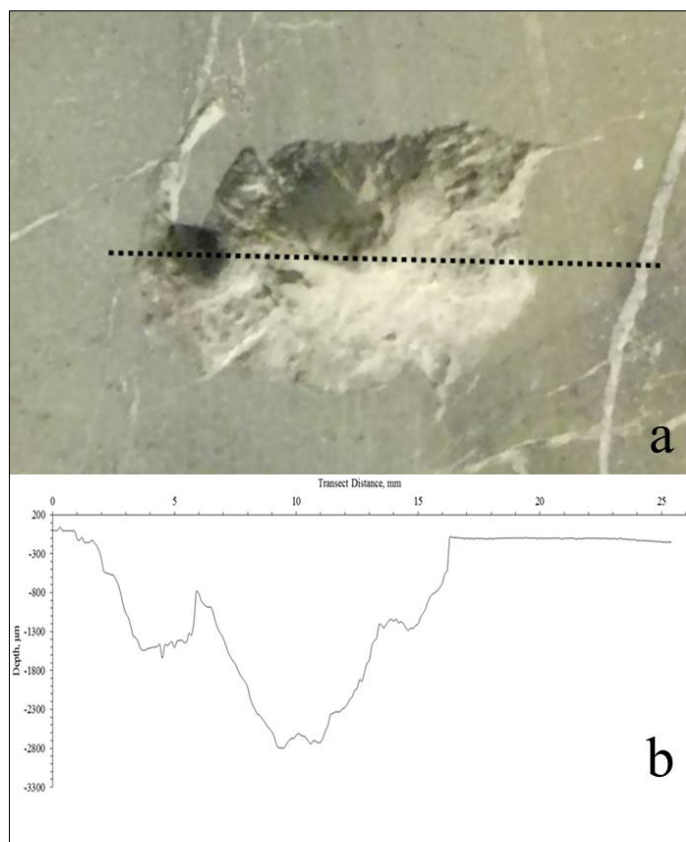


Figure 6.8: (a) an image of the Helen's bay sample with a dotted line depicting the route of the transect performed by the RLSS. (b) a depth profile of the crater, in the plane of the transect shown in (a). The depth profile was derived from the optimum focal position autonomously determined by the instrument.

The laser power used for each acquisition was between 25 and 50mW and the 50 μm spot was re-focused (using the autofocus system) onto the sample surface at each transect point. Dark frames were also acquired (using the same integration time) and subtracted from the CCD image.

To obtain spectra using the 632nm benchtop Raman instrument, the laser power was stabilised at 10mW and was focused onto a 38 μm spot on the surface of the sample. Integration times varied between 5 and 60s and multiple (10-30) images were stacked to produce each spectrum. Spectra were acquired from random positions within each area of interest as indicated in Figure 6.9.

For each spectrum, the signal-to-noise ratio (SNR) of the carbon G-band was calculated. Spectra with a carbon G band and an SNR value greater than 5 were considered for detailed analysis. For every band considered, the peak positions and widths were determined from (fluorescence) background subtracted spectra using centroid algorithms. The widths and positions of the carbon G bands were then plotted in order to identify clusters and trends that may indicate separate populations of carbon (i.e. that exhibit

differing levels of order), or that reveal information regarding the thermal history of the material.



Figure 6.9: An image of the crater produced in the surface of the Helen's bay sample. The blue spots highlight the regions from which spectra were acquired using the 632nm benchtop instrument.

6.2.5 RESULTS

RAMAN LASER SPECTROMETER SIMULATOR

Figure 6.10 shows an example of a spectrum acquired from the non-veinlet material surrounding the crater. Bands at 137cm^{-1} , 186cm^{-1} , 392cm^{-1} , 503cm^{-1} and 629cm^{-1} indicate the presence of anatase (noting that the sharp wavelength cut-off of the filter used in the RLS simulator allows for bands $<200\text{cm}^{-1}$ to be detected). Although they are weak, bands at 226cm^{-1} , 254cm^{-1} and 297cm^{-1} also suggest the presence of haematite. The corroborative band at 1324cm^{-1} also indicates the existence of haematite. The band at 1602cm^{-1} is the carbon G band (deriving from stretching of sp^2 bonded carbon atoms). In this spectrum the carbon D band is obscured by the 1324cm^{-1} haematite band, but its presence can be inferred from the shoulder on the right-hand side of the haematite band.

Figure 6.11 shows two examples of spectra obtained from the surface of the sample in the region of the crater. The upper spectrum reveals several strong signatures of calcite at 149cm^{-1} , 277cm^{-1} , 704cm^{-1} and 1082cm^{-1} . The strongest anatase band is visible again at 137cm^{-1} , along with three other bands (with low SNR) around 390cm^{-1} , 560cm^{-1} and 630cm^{-1} .

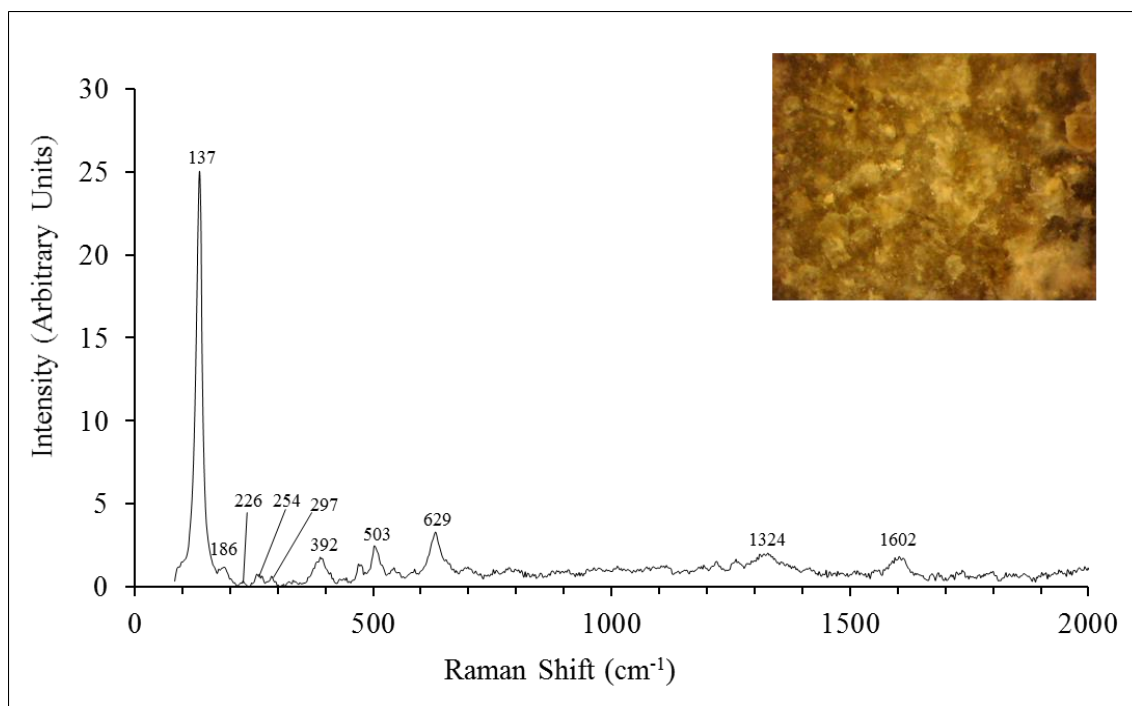


Figure 6.10: An example spectrum acquired from the unaltered material (surrounding the crater that does not include a white veinlet). The insert shows a close-up image of the material obtained using the integrated context imager within the RLS simulator.

The lower spectrum contains stronger signatures of anatase, as well as bands at 297cm⁻¹ and 1329cm⁻¹, indicating the presence of haematite. The carbon G band is also present

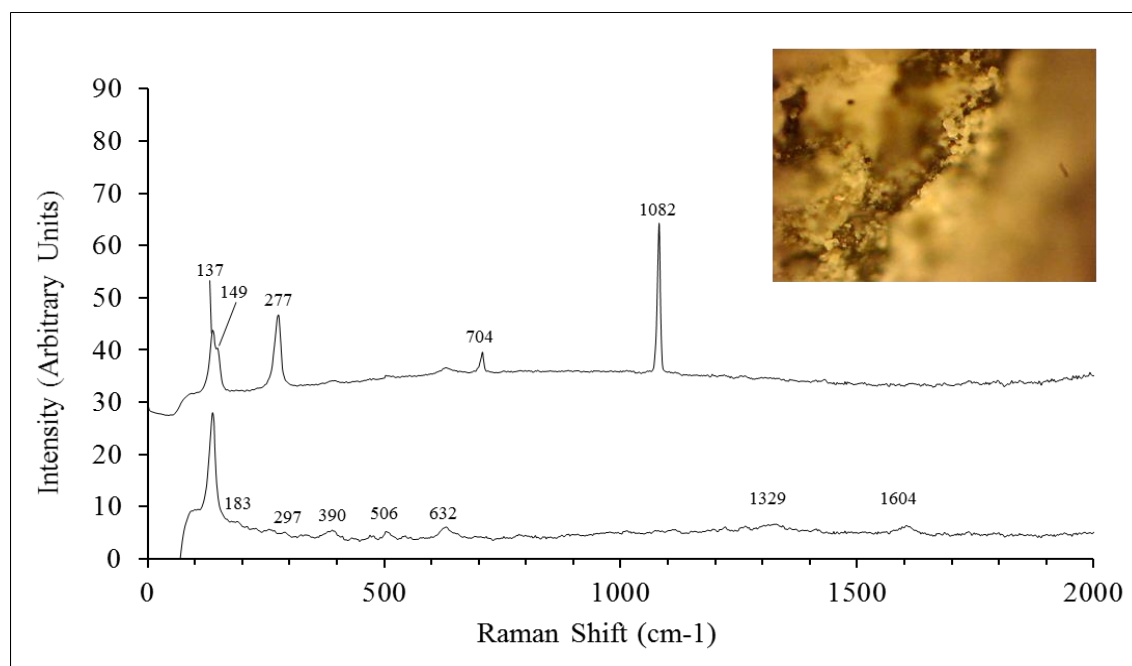


Figure 6.11: Two examples of spectra obtained from within the crater using the RLSS. The insert shows an image acquired using the integrated context imager. The out of focus part of the image shows that the surface of the sample is very variable within the crater.

however, there is little evidence of the carbon D band near the low SNR 1329cm^{-1} haematite band.

An example of a spectrum acquired from the veinlet material can be seen in Figure 6.12. A strong band at 137cm^{-1} and three weaker bands at 390cm^{-1} , 506cm^{-1} and 632cm^{-1} are again indicative of the presence of anatase. The band at 470cm^{-1} may result from the presence of quartz. However, the signal level is insufficient to identify corroborating bands. Once again, the carbon G band is clearly evident, with a greater signal-to-noise ratio compared to the spectra obtained from either the crater or the unaltered material. The band at 1322cm^{-1} is likely to result from haematite; however, there are no additional haematite bands apparent in the data. There is evidence of a shoulder on the 1322cm^{-1} band (around 1358cm^{-1}) which probably results from the carbon D band.

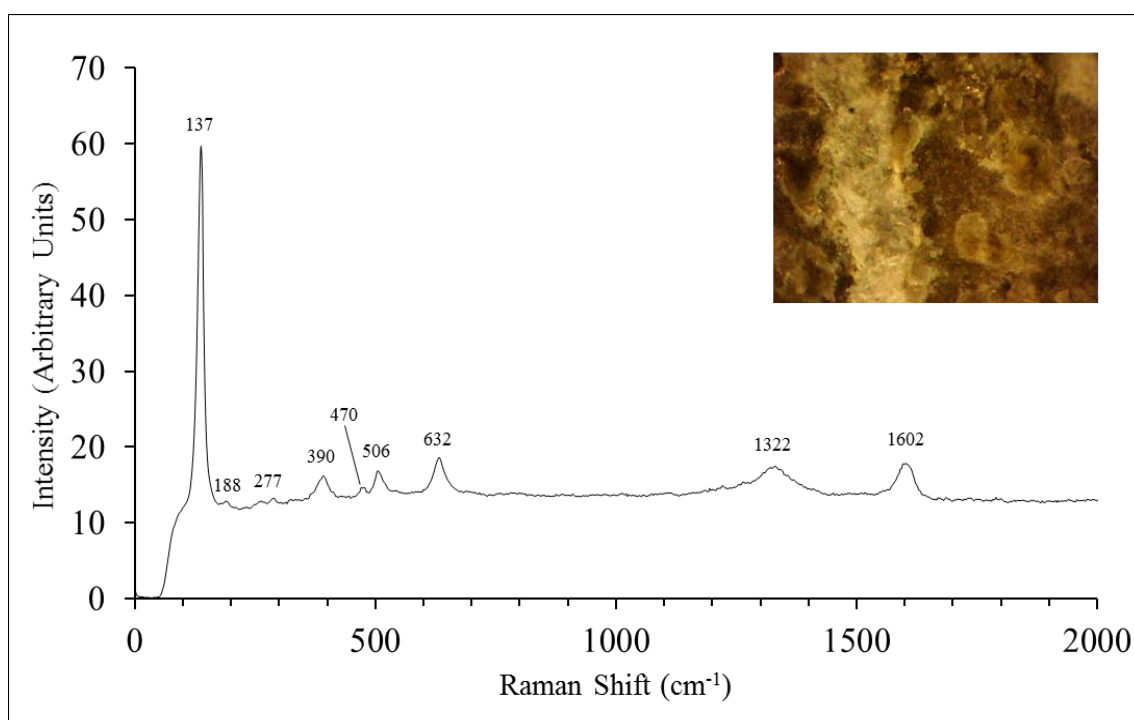


Figure 6.12: A Raman spectrum obtained from a white veinlet on the surface of the Helen's bay sample. The insert shows that white material (running down the left of the image) clearly is distinguishable from its surrounding, even on a micron scale.

Figure 6.13 shows a cross plot of the position and the FWHM of the carbon G bands seen in each spectrum. The plot contains points from 9 separate places in the unaltered material surrounding the crater, 7 bands from within the crater region and 5 different locations on the white veinlet material. The plot also shows the average carbon G band position and

FWHM from each area of the three regions of interest (as well as the standard deviation of each parameter within the sample set).

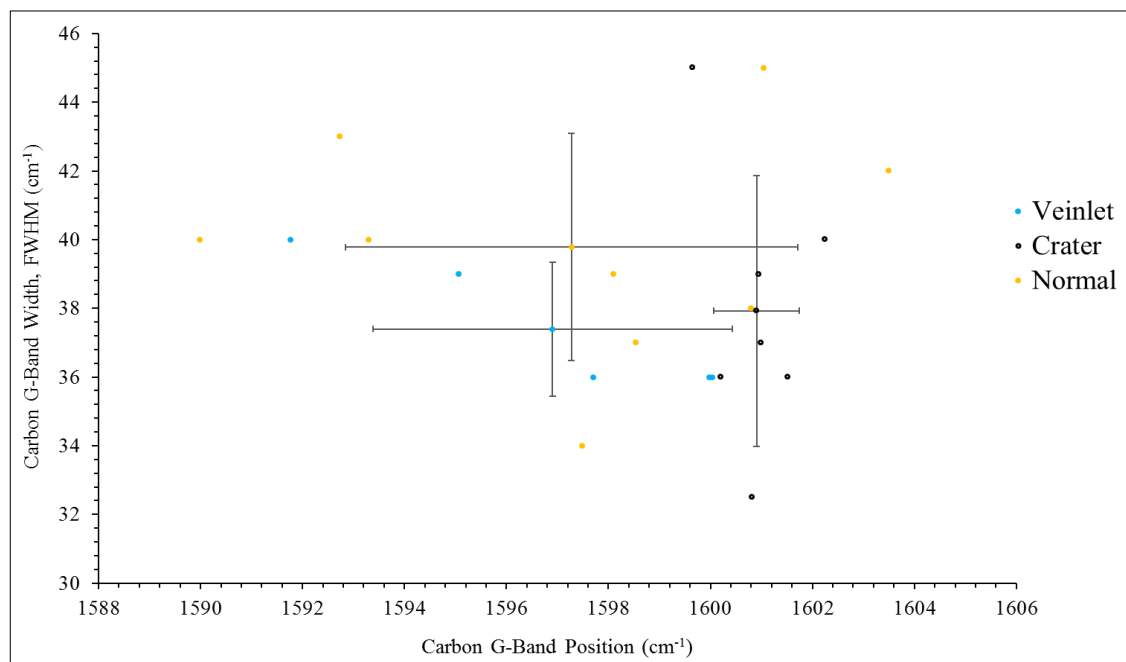


Figure 6.13: A cross plot of the Raman shift and FWHM of each carbon band acquired from the three areas of interest.

Figure 6.14 shows a modified version of the cross plot featured in Figure 6.13. For clarity, the data from the veinlet material has been removed, clearly showing the contrast between the crater material and the un-impacted bulk material.

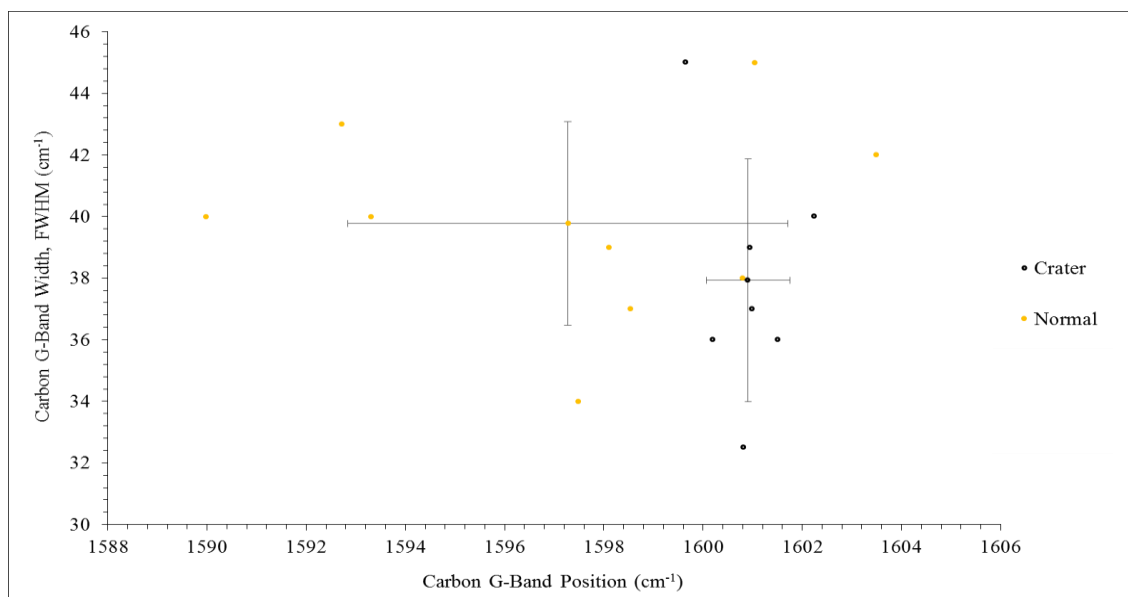


Figure 6.14: A cross plot of the Raman shift and FWHM of each band observed in the crater and unaltered bulk material of the sample.

CRATER AND EJECTA ANALYSIS AT 633NM

The 632nm benchtop instrument was used to acquire comparative spectra from the crater and the ejecta material. Figure 6.15 shows an example spectrum acquired from the crater material on the surface of the Helen's Bay sample. The spectrum shows bands at 396cm^{-1} , 513cm^{-1} and 637cm^{-1} indicative of anatase. However, unlike the RLS simulator, this spectrometer does not have the capability to detect bands lower than $\sim 150\text{cm}^{-1}$. Therefore, the strongest anatase band at 138cm^{-1} is not detectable. The small band at 479cm^{-1} could be due to the presence of quartz, but this cannot be confirmed without the confirmation of additional bands. The small band at 1088cm^{-1} could indicate the presence of calcite in the sample. Finally, the spectrum also contains a band at 1601cm^{-1} , associated with the carbon G band and a band at 1327cm^{-1} , which is likely to originate from haematite.

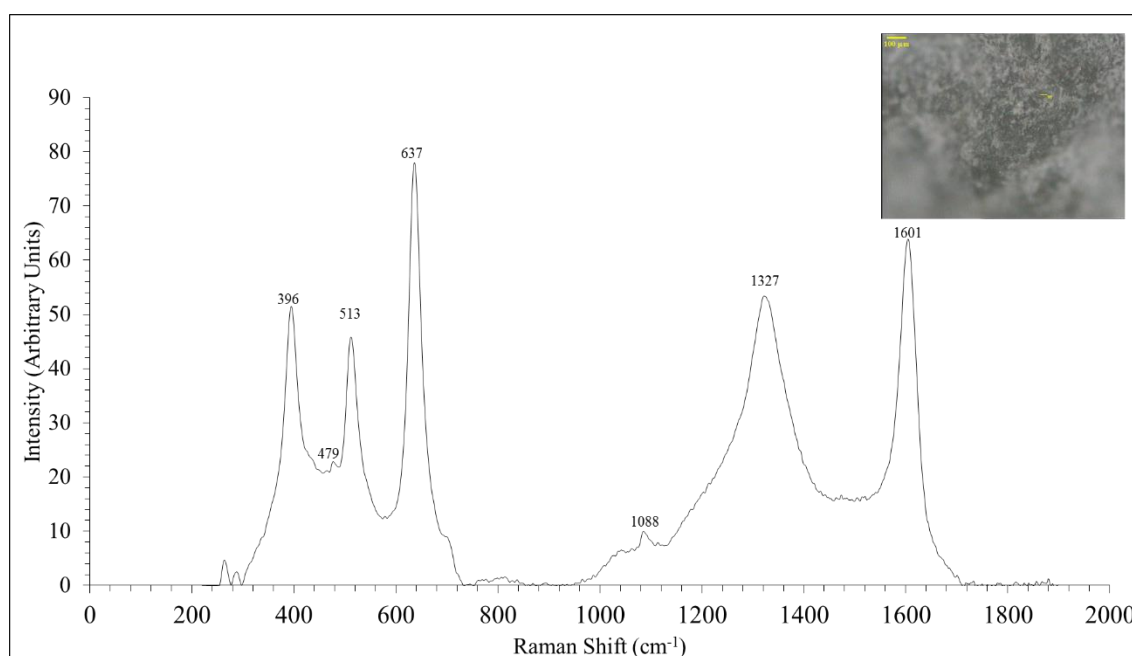


Figure 6.15: An example spectrum acquired from the crater material using the bench top prototype instrument located at the Centro de Astrobiologia in Spain. The insert shows a microscopic image of the sample area from which spectrum was acquired.

Figure 6.16 shows an example of a Raman spectrum obtained using the 632nm instrument from ejecta material generated by the impact process. The spectrum contains three strong anatase bands at 197cm^{-1} , 396cm^{-1} , 513cm^{-1} and 638cm^{-1} . Similar to the data presented in Figure 6.15, the spectrum obtained for the ejecta contains a band at 478cm^{-1} which is expected to originate from quartz in the sample. The strong band at 1602cm^{-1} is the carbon

G band. However, the carbon D band is not visible above the strong haematite band at 1320cm^{-1} . The weak band at 287cm^{-1} is also likely to be a haematite band.

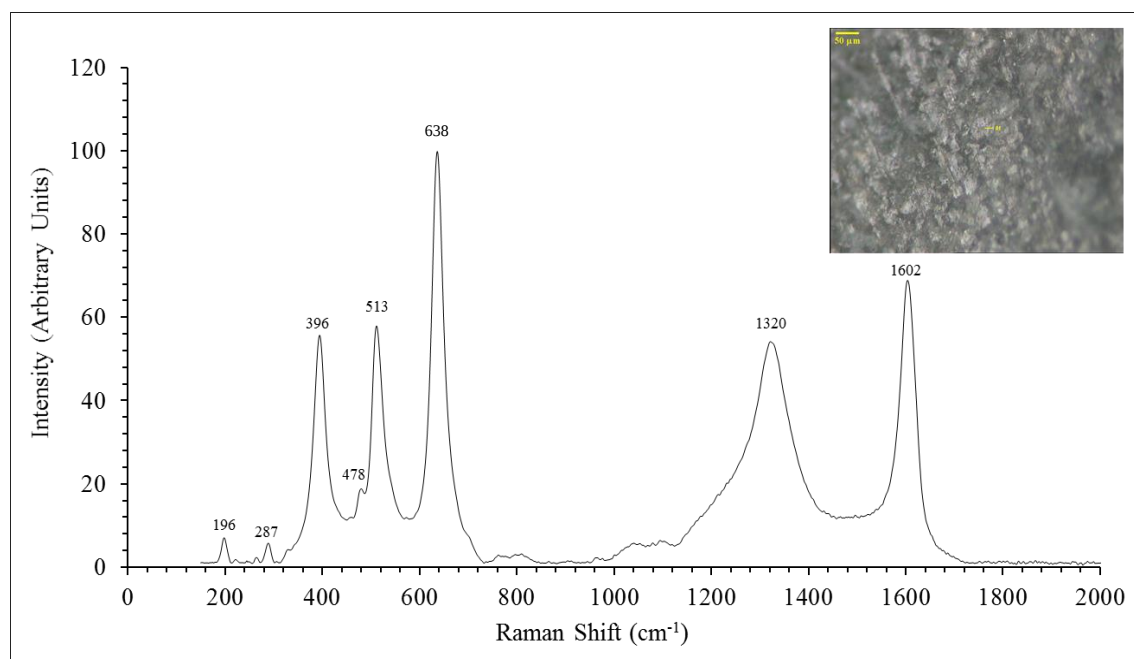


Figure 6.16: An example spectrum obtained from the ejecta material using the 632nm Raman instrument. The insert contains a microscope image of the ejecta material.

Figure 6.17 shows the cross plot derived from the positions and widths of carbon G bands within the spectra obtained from the crater and ejecta material. The plot contains the

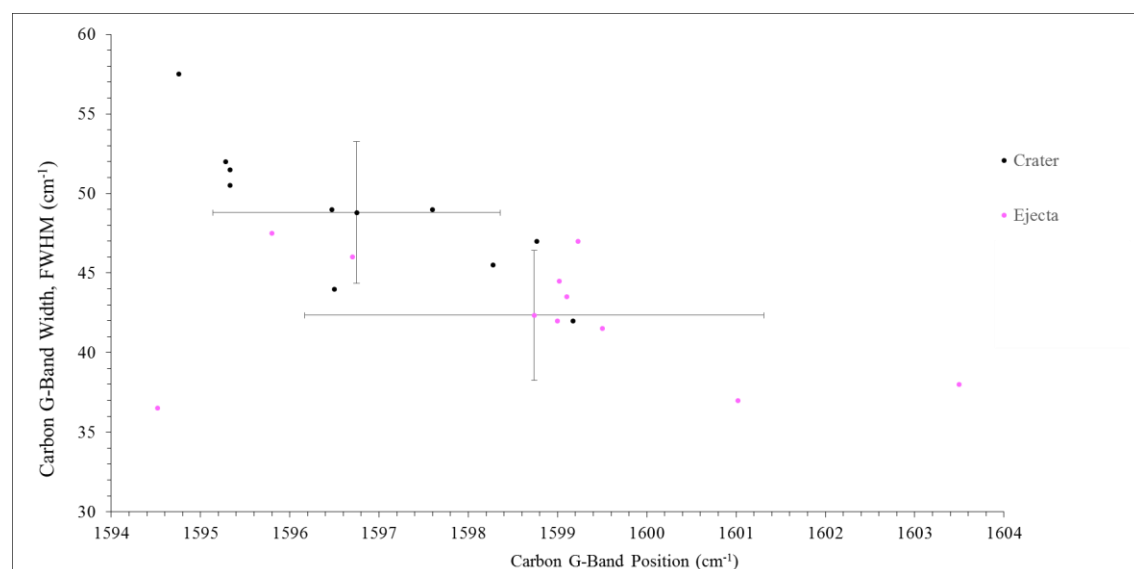


Figure 6.17: A cross plot composed of the carbon G band positions and widths obtained from the crater and ejecta material using a 632nm Raman spectrometer.

positions and widths acquired from 10 separate measurements in each area along with the average and standard deviation of each data set.

6.2.6 DISCUSSION

The reduced carbon study aimed to not only detect, but also characterise the carbon in a meteorite analogue sample using the RLS simulator and a benchtop Raman instrument, since carbon has been identified as a key target for ESA's ExoMars mission.

A number of spectra were acquired from the crater, white veinlets and unshocked material surrounding the crater using the RLS science simulator. Spectra containing carbon G bands were isolated and the band positions and FWHM's were calculated using centroid algorithms. The position and FWHM of each carbon G band detected were then plotted in order to try and identify different populations. Figure 6.13 shows the characteristics of each carbon band detected by the RLS simulator for all three sites of interest on the surface of the sample. The plot shows that a broad range of band positions and widths were measured from all sites. However, it is also clear from the plot that there are three distinctive groups of carbon material. It can be seen that the carbon bands generated by veinlet material generally (on average) exhibit lower band positions compared to those in the crater material. The plot also shows only a small overlap of 0.3cm^{-1} between the two groups. It shows that the average width of the carbon G band in the veinlet material is lower than the unaltered material suggesting it can be readily differentiated from the bulk material in the sample.

The characteristics of the carbon present in the crater material, seen in the plot, can be distinguished from the bulk material in terms of band position. Although the carbon in the unaltered material spans a relatively large range of positions and widths (with an average position of $1597 \pm 4.4\text{cm}^{-1}$ and an average width of $39.8 \pm 3.3\text{cm}^{-1}$), the observed cratered material is grouped towards larger wavenumbers with an average of $1601 \pm 0.8\text{cm}^{-1}$. The carbon detectable in the crater also exhibits slightly smaller widths (on average) compared to the unaltered material, although the scatter of the crater material in terms of position is still within the error bars of the unshocked material meaning the groups are not completely separable. These findings are consistent with work performed by Wickham-Eade & Burchell (2017), who concluded that the width of shocked basalts decreases. The study also showed that the wavenumber of the carbon G band in basalt

increases compared with those observed in unaltered basaltic material. This alteration in the band characteristics suggests the increase in thermal maturity presents as stronger molecular bonding in the material.

Figure 6.17 shows a cross plot of carbon G band characteristics observed in spectra acquired from the crater material and ejecta material. The spectra were acquired using the 532nm benchtop instrument described in Section 6.3.3. The cross plot shows that the average carbon G band position observed in the crater using the 532nm instrument was $1596 \pm 1.6\text{cm}^{-1}$, with an average width of 49.4cm^{-1} . In contrast, the average position of the carbon G band observed in the ejecta material was $1598 \pm 2.5\text{cm}^{-1}$ with an average width of $42.3 \pm 4.08\text{cm}^{-1}$. It is evident from Figure 6.17 that there are two distinct carbon populations significantly separated in terms of the observed bandwidth (the populations only overlap by 2.1cm^{-1}). In comparison to the work produced by Wickham-Eade & Burchell (2017), the plot implies that the ejecta material has increased in thermal maturity compared to the crater material. However, the two populations do overlap considerably in terms of observed positions, highlighting that both band parameters should be measured to ensure the band was assigned to a particular thermal maturity.

7 INSTRUMENT FIELD TESTS

Between the design and development stages and its deployment into space, it is paramount to gain a realist and detailed insight into how an instrument will perform once it has reached its destination. To access the success of a proposed instrument (for instance, while it is still in its early stages of development) it is subject to a number of analogue missions (Olson and Craig, 2011). These missions provide a platform to demonstrate the suitability of and stress the instruments' configuration, planned operating modes and scientific performance in the context of a harsh, non-laboratory environment and on realist samples, more comparable to those it will encounter at its final destination.

As planetary missions became more ambitious (and therefore challenging and expensive), a large amount of effort has been applied to identifying terrestrial analogue sites: locations on Earth that bare some geological, mineralogical or climatal resemblance to the mission landing site in order to realistically test the limits of analytical space instrumentation. Suitable analogue sites are selected primarily based on their terrain, rock distribution and the physical characteristics of the soils in the area, while also accounting for ease of personnel access, equipment and maintenance facilities and safety (Sanders *et al.*, 2011). For example, Mauna Kea in Hawaii is a recognised analogue site for Lunar ISRU missions (see Figure 7.1 (a)). The high altitude terrain exhibits fine basaltic regolith, volcanic rock fragments (Wettergreen *et al.*, 2010) and a large abundance of minerals and oxygen confined to the soil (as a results of the prolonged volcanic activity) (Olson and Craig, 2011).

In terms of Mars analogue sites, the Rio Tinto (river) region in south-western Spain (featured in Figure 7.1 (b)) exhibits extensive mineral deposition incorporating sulphates such as jarosite, halotrichite, copiapite and gypsum, a number of which were observed on the surface of Mars by the Opportunity rover (Squyres *et al.*, 2006). The river provides a hydrothermal, iron and sulphur enriched environment in which microbial colonies thrive.

Pigments such as ferrihydrite and iron oxyhydroxide produced by the bacteria have turned the waters of the Rio Tinto a deep blood-red (Edwards *et al.*, 2007).

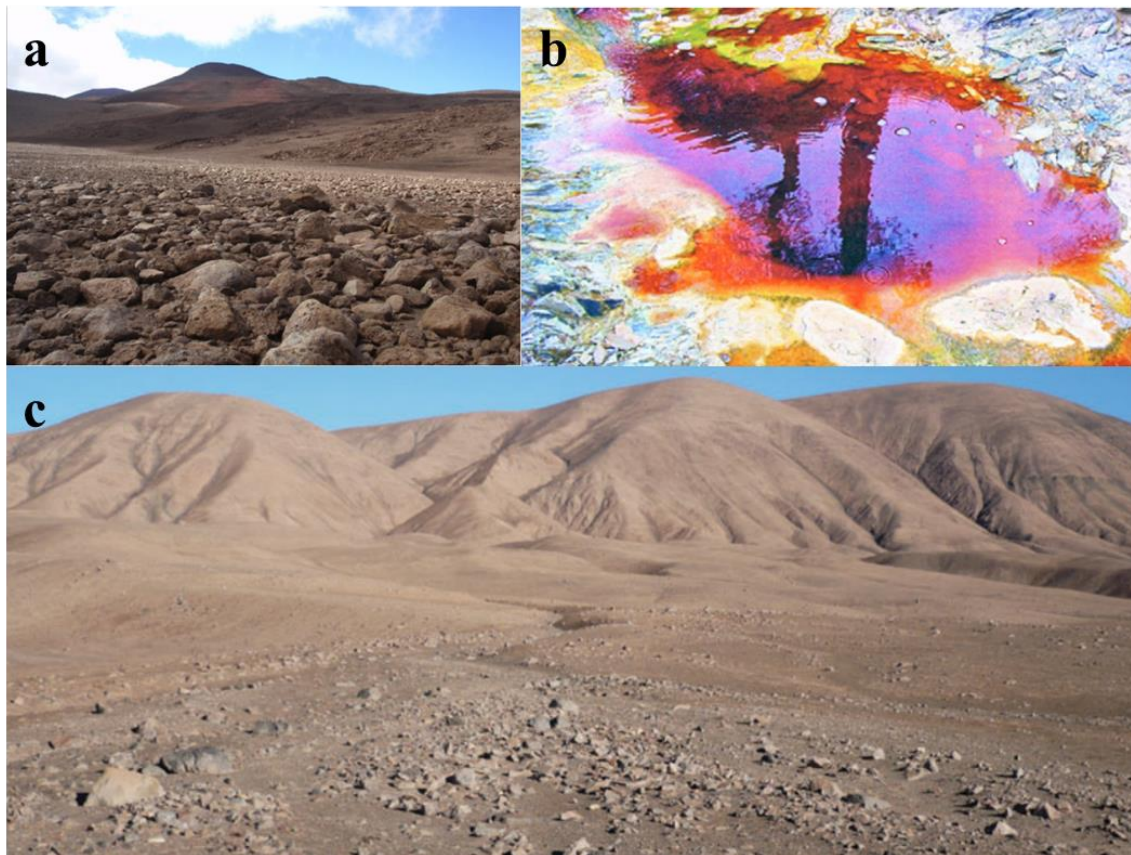


Figure 7.1: (a) An image of the Apollo valley at Mount Mauna Kia, Hawaii. Credit: (Graham *et al.*, 2015). (b) A photograph of a mineral pool in the Rio Tinto region in Spain. Credit: (Edwards *et al.*, 2007). (c) A photograph of a mountain base west of the Salar Grande, the Atacama Desert, Chile. Credit: (Parro *et al.*, 2011).

In South America, the hyperarid planes of the Atacama Desert stretches for 600 miles from southern Peru into Northern Chile. The region receives <10mm of precipitation per year (Preston, Grady and Barber, 2012) making it an ideal Mars analogue. The local mineralogy includes quartz, calcite, albite and haematite (Stalport *et al.*, 2012), all of which have been detected on the surface of Mars. The vast terrain also features many resemblances to the red planet including gully structures, which have been observed on Mars during the past decade (Malin *et al.* 2006). Geological features such as these are the key to understanding the origin of water in such environments (Heldmann *et al.*, 2010). Figure 7.1 (c) shows a Martian-like plane situated west of the Salar Grande. However the most studied feature of the Atacama is its ability to harbour life, namely extremophiles (Wierzchos, Ascaso and McKay, 2006; Cabrol *et al.*, 2007; Kuhlman *et al.*, 2008). Despite the extensive dryness, extreme temperatures (-23 to 23 °C.) and high solar

irradiance, trace amounts of bacteria have been detected thriving in the desert soil (Navarro-González *et al.*, 2003). As part of the preparation of ExoMars in 2020 (see Chapter 1 for a full description), organics and suggested biomarkers from extremophilic bacteria were detected using miniaturised Raman Spectrometers, not dissimilar to the RLS instrument (Vítek *et al.*, 2012).

In coordination with the instrument development detailed elsewhere in this thesis, this chapter describes two field campaigns, in which the performance of particular Raman instrument configurations were tested and characterised in non-laboratory environments. The first campaign was the Mars Utah Robotic Field Investigations mission (MURFI) and the second was the MIne Analogue Research (MINAR) programme. Both missions took place in difficult to access and dusty terrains and not only provided samples of mineralogical relevance to Mars mission preparations, but also two extreme, yet contrasting test environments. This chapter describes the individual environments, their location, the aims of the scientific studies and the instrumentation deployed in each trial. Series of Raman spectra acquired from a range of analogue samples identified at each site are then described.

The spectra acquired during the field test campaigns were then used in conjunction with the instrument model described in Chapter 3, to simulate the performance of 5 specific instrument configurations (operating in various conditions) when acquiring spectra from samples similar to those found in the field locations. The chapter then discusses how the derived instrument performances can be used to inform future Raman instrumentation development and how preparations could be optimised for future field test campaigns.

7.1 MODEL DESCRIPTION

Chapters 5 and 6 of this thesis have described how the radiometric model detailed in Chapter 3 can be used to predict the spectral signal-to-noise ratios (SNR) achieved by a particular configuration of Raman instrument in a given experimental scenario. The model uses known instrument performance characteristics (such as subsystem or component throughput) and geometry to predict the signal and noise levels achieved in a

particular operating mode. The modelled SNR values can then be used to compare and contrast the performance of particular instruments and particular acquisition strategies.

In this chapter, the instrument model is used to estimate the performance of 5 separate instrument configurations (using samples representative of the material likely to be encountered) in a range of different field environments (in both darkness and a medium level of ambient light). The model is also used to evaluate the performance of a further 5 stand-off instruments operating at 4m from the sample in medium ambient light conditions (i.e. for applications where it would be advantageous to analyse material on a nearby incline or rock face). For both field trials, spectra were acquired using an in situ Raman instrument spectrometer that uses a non-gated detector and a continuous laser. Radiometric values were then extracted from the data and used in the model. Specific details regarding the instruments used to acquire the data are given in Sections 7.2.3 and 7.5.3 of this chapter.

Table 7.1 summarises each configuration modelled in this chapter. A full description of the system geometries can be found in Chapter 3, Section 3.1.1.

The five configurations vary in terms of laser type, detector type/mode of operation and optical configuration. For the laser options, a particular configuration includes either a pulsed laser or a continuous laser. Configurations 2 to 5 and 7 to 10 are modelled using the Surelite I laser developed by Continuum, Nd: YAG laser that operates at 532nm and produces 5ns pulses at an energy of 35mJ per pulse. The continuous laser estimates are based on the performance of the Excelsior DPSS continuous wave 532nm laser (a full description of both lasers is given in Section 3.1.2 of Chapter 3).

In terms of the detector systems, the model simulates gated, non-gated, gated and clock-shift systems. For the non-gated systems, the model uses the characteristics of a Sony ICX285AL Exview coupled with a continuous laser and a back illuminated, AIMO CCD42-10 with a pulsed laser. This device was chosen following a trade-off between dark current, QE and detector size (discussed in detail in Chapter 2, Section 2.2). The model assumes that both detectors operate in a ‘static stare’ mode in configurations 1, 2, 6 and 7. In this mode, the devices collect charge for a period of time equivalent to the integration time that was used to acquire the initial spectra, after which the device is read out and the signal is measured.

Configuration no.	Working distance/ cm	Collection geometry	Laser type	Detector type	Detector Operation
Ambient Light Level: 0/ Medium					
1	2.5	Co-axial	Continuous	Sony CCD	Non-Gated
2	2.5	Oblique	Pulsed	CCD42-10 BI AIMO	Non-Gated
3	2.5	Oblique	Pulsed	CCD42-10 BI AIMO	Shift Operation (1)
4	2.5	Oblique	Pulsed	CCD42-10 BI AIMO	Shift Operation (2)
5	2.5	Oblique	Pulsed	CCD30-11	Gated
Ambient Light Level: Medium					
6	400	Co-axil	Continuous	Sony CCD	Non-Gated
7	400	Oblique	Pulsed	CCD42-10 BI AIMO	Non-Gated
8	400	Oblique	Pulsed	CCD42-10 BI AIMO	Shift Operation (1)
9	400	Oblique	Pulsed	CCD42-10 BI AIMO	Shift Operation (2)
10	400	Oblique	Pulsed	CCD30-11	Gated

Table 7.1. A table summarising 6 different instrument configurations, the theoretical performances of which are considered in this chapter.

The model simulates the clock-shifting mode using the characteristics of a back illuminated, AIMO CCD42-10 device. The first shift operation utilises fast continuous readout similar to TDI operation (see Chapter 2, Section 2.2.1). In this mode, charge is continuously shifted through the device and read out at maximum speed. Every 0.1 seconds (every~140 rows), the device will capture the Raman signal generated by a laser pulse. This operation provides a short window of data acquisition which also corresponds to a small window of ambient light acquisition (a significant source of noise). When used in high ambient light environments this operation should allow for a fraction of the ambient light to be acquired while still capturing all of the signal.

The second shift mode operates in a similar way to the first. However, the speed at which charge is shifted down the device is not limited by the readout speed. In this second shift mode, charge is rapidly shifted down the device to the read out register. Pixels prior to those containing data, are not read out. By shifting a row every 15 μ s, charge stays in the image pixels for a minimum amount of time, meaning dark current is minimised compared to the first shift operation. The use of this operating mode also means the pixels containing Raman signal can be read out slower than those continuously read out in clock-shift operation which improves the system read noise.

The performance of the gated system is modelled using parameters appropriate for the PI-MAX4 camera developed by Princeton Instruments. The PI MAX uses a CCD30-11 manufactured by e2v (further details are provided in Chapter 2, Section 2.2.7). The estimated dark noise for the device was calculated assuming that the CCD30-11 detector is read out as fast as possible to minimise dark current build up. The model assumes that the incorporation of a gated detector with a pulsed laser allows the instrument to temporally avoid fluorescence and it therefore has a negligible impact on the signal-to-noise ratio.

When estimating the performance of a Raman system operating over a distance of 4m, the model assumes that configurations 6 through to 10 employ a 12.5cm reflector telescope, identical to that described in Chapter 3, Section 3.1.3. To simulate in situ systems, the model uses the parameters of the Kaiser Optical Systems MultiRxn Probe also described in full in Chapter 3, Section 3.1.3.

7.2 PLANETARY ANALOGUE MISSION 1: MARS UTAH

ROBOTIC FIELD INVESTIGATIONS

7.2.1 MISSION OVERVIEW

In preparation for ESA's ExoMars rover mission (due to launch in 2020), the UK Space Agency (UKSA) conducted its first mission simulation campaign: The Mars Utah Robotic Field Investigation (MURFI), in late 2016 (Balme *et al.*, 2017). In collaboration with the Canadian Space Agency, fifteen institutions from around the UK (the Open University, the UK Science & Technology Facilities Council (STFC), Imperial College London, University of Oxford, University of Leicester, Mullard Space Science Laboratory, University of St Andrews, University College London, Birkbeck University of London, Aberystwyth University, the Natural History Museum, London and the University of Cambridge) participated in a four week long campaign that aimed to simulate the upcoming ExoMars rover mission operating scenarios. The project simulated two major aspects of a planetary rover mission: (i) the deployment of a mobile platform (equipped with scientific instrumentation) in a harsh (Mars analogue) environment and (ii) the operation of a robotic platform from a remote location using only information and data collected by the on-board rover instruments, in order to meet a pre-defined set of science goals.

The mission ran from the 24th of October to the 14th of November, 2016, and was completed by two teams: the Science and Operation Team (SOT), who were based at the Mission Operations Centre (MOC) at the Harwell Campus in the UK and a Field and Rover support team who were located at a desert field site in Utah, USA. The campaign was designed to train UK scientists and engineers in mission operations in order to support future planetary exploration and to gain experience in implementing extensive field trials. MURFI also provided an opportunity to establish a UK-based Rover Operations Centre- a platform for developing collaborations between institutions (within and outside the UK) and with other space agencies. The project aimed to develop the key skills of UK scientists, such as remote science interpretation, tactical planning and working with limited resources and data. Furthermore, the MURFI project provided an opportunity to work with a collection of instruments that very closely resemble those on the ExoMars rover.

During the first week of the trial, the SOT used remote sensing data to simulate the view HI-RISE (a High Resolution Imaging Science Experiment) provided of the Martian landscape. Using only orbital images, the SOT team performed initial mapping of the ‘landing site’ in order to identify potential science targets, hazards and possible traverses. The rover platform and its instrumentation were also setup, tested and characterised in this first week (including the Raman instrumentation detailed in this thesis). The following weeks were dedicated to following an ExoMars-like mission profile, in which the team located at the Harwell campus guided the rover to destinations (chosen based on instrument data) in order to assess the mineralogy and geology of the terrain.

7.2.2 SITE

The MURFI ‘landing site’ was located 7.5 km north-west of Hanksville, USA, at an altitude of ~1350m. Figure 7.2 shows the landing site and its location to Hanksville. The

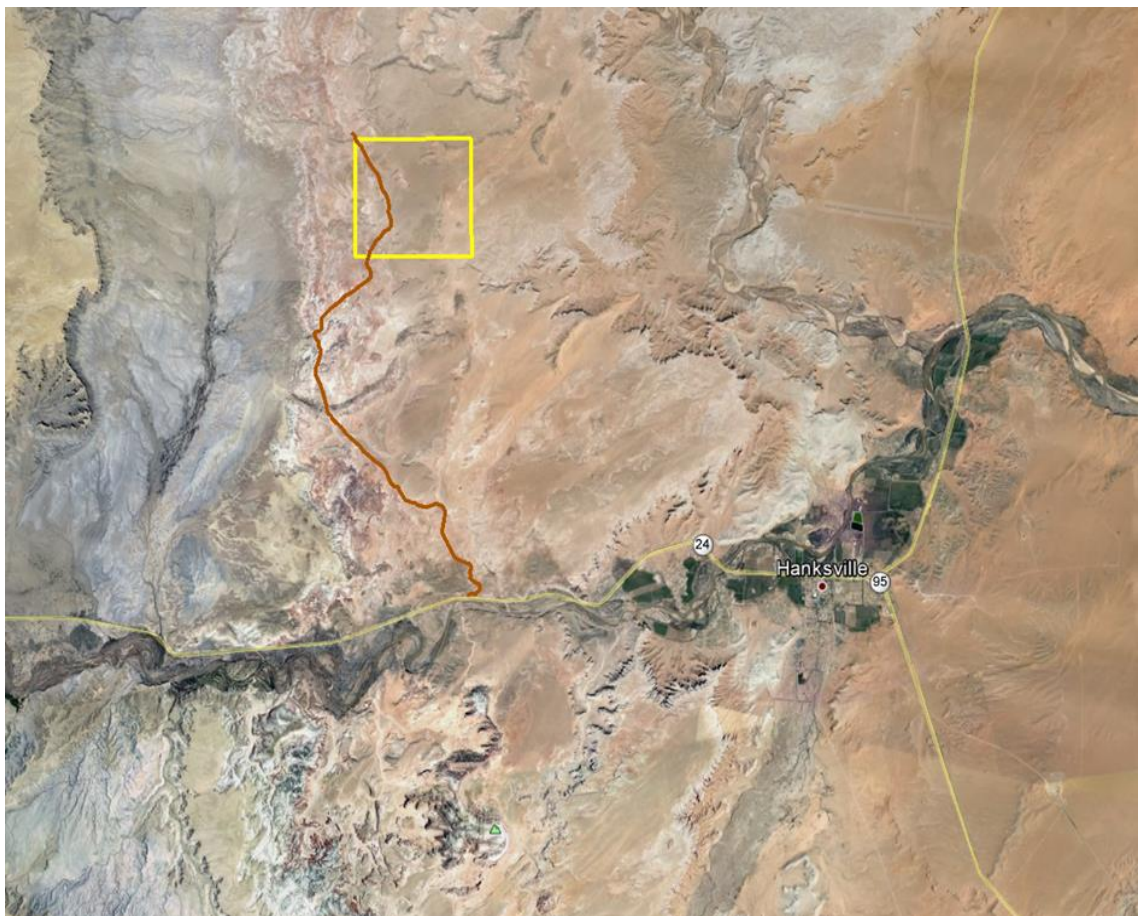


Figure 7.2: A Map of the areas Surrounding Hanksville, Utah, USA. The map details the route from the main roads to the MURFI landing ellipse, outlined by the yellow square. Map Credit: Google.

region's climate is arid, with temperatures range from 37.1°C in July to -10.9°C in January and annual precipitation reaches around 141mm (10% of which is snow) (Clarke *et al.*, 2011).

The geology and minerology of the region has been assessed extensively in the past (Clarke J.D.A and Pain, 2004; Kotler *et al.*, 2011) and it has become a recognised Mars analogue site (Chan *et al.*, 2004). The area surrounding the landing site consists of sandstone and shade (textured rock) regions rich in clay. One of the main features of interest in the area is the presence of fluvial channels, similar to those observed on the Martian surface (Newsom, Hagerty and Thorsos, 2001). In mineralogical terms, materials such as quartz, calcite and sulphate evaporates (such as gypsum) have been observed (Vaniman *et al.*, 2014), many of which are significant for the preservation of microfossils. In addition, iron oxides such as haematite, exist in small, spherical structures, indicative of the formation and geological history of the area. Similar iron oxide structures were detected by the Opportunity rover in the Meridiani Planum region on Mars (Glotch *et al.*, 2004).

7.2.3 ADAPTED RAMAN INSTRUMENTATION

The MURFI field site activity provided an opportunity to test and characterise the Raman instrumentation developed in this thesis in a challenging, hostile environment similar to that expected on a planetary surface. The Raman instrument was deployed on the 31st of October 2016 and tested during the subsequent 2 days. The system was set up and operated in an open, outdoor space between the hours of 09:00 to 16:00. During this time the ambient light levels were very high (from the unobscured sun light) and the ambient temperature ranged between 14°C and 25 °C. The immediate terrain at the site (shown in Figure 7.3) consisted of fine, lightweight soil grains, which generated a dusty environment. The contrasting environment of the Utah desert (compared to the laboratory) meant that a number of alterations had to be made to the standard instrumentation in order to not only maximise performance (by keeping noise levels minimised) but to meet the restrictions of the campaign such as low mass, power and data exchange constraints.



Figure 7.3: The MURFI field site, Utah, USA. The photograph shows the edges of the flat terrain instrument testing took place.

The Raman system used for the MURFI field trial was based on Configuration 4, detailed in Chapter 3, Section 3.1.1 (see Configuration 1 in Table 3.1), and shown in Figure 7.4. This system was chosen since it was the most miniaturised, light-weight and robust configuration (in comparison to the other configurations described in Chapter 3). The system is also the most representative of the ExoMars RLS instrument and therefore met the MURFI mission aims of demonstrating ExoMars-like instrumentation.

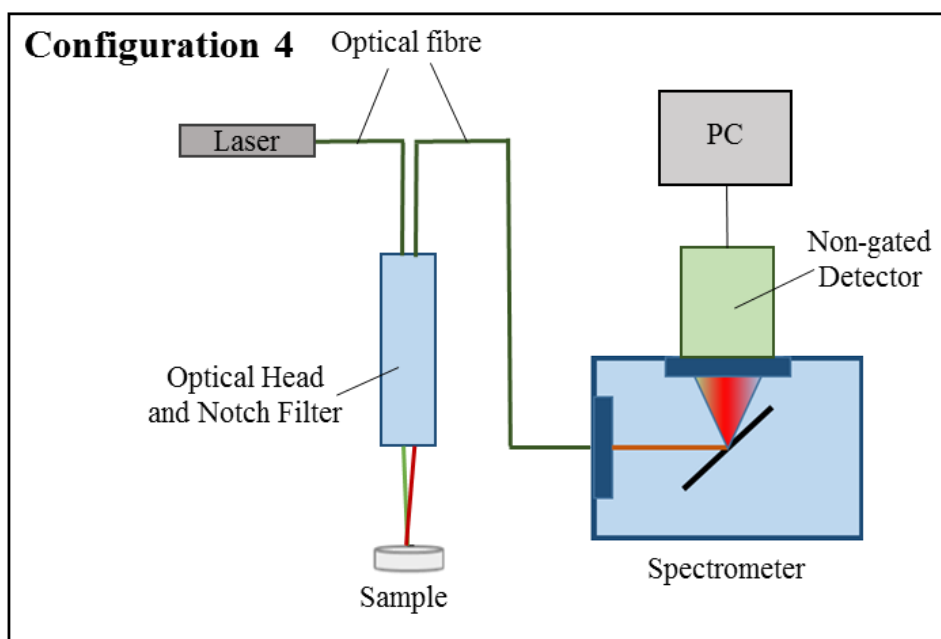


Figure 7.4: A diagram illustrating the layout of the Raman instrument deployed in the MURFI field trials. The configuration is based on Configuration 4 (detailed in Chapter's 3 and 4)

The excitation source was an Excelsior DPSS continuous wave laser which provided 60mW of power at 532nm. The laser light was focused into an optical fibre using an M-10X microscope objective (shown in Figure 3.7, Chapter 3, Section 3.1.2), both of which were secured to an optical slab. The logistics of the field trip prevented the use of a power meter (a device usually used to maximise the alignment of the laser optics), therefore alignment was completed prior to the trip, in the laboratory. The laser optical system was aligned to achieve a maximum throughput of 45mW at the end of the optical fibre. The laser and its associated optics were confined to a lightweight container to prevent dust and debris build up on the optical components (which would reduce the amount of laser light incident on the sample and therefore reduce the Raman emission).

The laser excitation source was focused onto a sample using a Kaiser Optical Systems MultiRxn Probe. Laser light is concentrated into the top of the probe, via the fibre optic and is directed through a notch filter. The probe encompasses an 8.0mm wide exit

compound lens, which focuses the laser light into a 0.5mm wide spot on the sample, 25.0mm from the end of the probe. A full description of the probe head and its internal components is given in Chapter 3, Section 3.1.3. Optical head and sample were kept uncovered and exposed to ambient light to simulate its potential placement on the arm of a rover. In this configuration, the optical head would be coupled via an optical fibre, to the spectrometer, which would hypothetically be housed in the body of a rover.

The light scattered (both elastically and inelastically) by the sample was collected by the MultiRxn Probe at an angle of 180degrees to the excitation source. The collected light was filtered by the notch filter, which rejects >99% (for measurement details see Chapter 3, Section 3.2) of the photons at 532nm, i.e. the Rayleigh scattered laser light. The filtered light was focused into a secondary optical fibre located towards the top of the probe head, parallel to the laser fibre.

The system spectrograph was a Kaiser Optical HoloSpec spectrograph, which comprised a collimating lens, a holographic diffraction grating and a moveable camera lens (to allow for focusing). Each of these components is described in full in Chapter 3, Section 3.1.4. This spectrometer, which is usually integrated into the ExoMars RLS prototype system located at the University of Leicester, was the preferred choice for the field-ready system as it has a sufficiently large spectral range (175 cm^{-1} to 4400 cm^{-1}). It is also transportable as a single unit (with each component pre-aligned and fixed to a single optical plate) and is contained within an almost light-tight cover to minimise unwanted ambient light entering the system.

The camera system used in this configuration was a commercial off-the-shelf CCD system manufactured by Starlight Xpress, shown in Figure 7.5. The system incorporated a ICX205AL Sony SuperHAD interline CCD detector, a 6.4mm x 4.75mm device with a 1392 x 1040 pixel array. Each pixel is $4.65\mu\text{m}$ in size, has a full well capacity of 20,000 e^- and has a quantum efficiency of ~50% at 520nm and 30% at 420nm. At a temperature of 10°C , the dark current is less than 0.1 e^- per second and the associated electronics provide ~7 e^- read noise.

This particular detector system was chosen for several reasons. Firstly, the system was air cooled, light weight (50g) and encapsulated in a light-tight casing. The system also had low power requirement (maximum of 2.5W), making it ideally suited to the low

resource field site. The entire system was light weight. The camera was aligned with the spectrometer and both were kept in an enclosure layered with optical cloth (cloth that is highly absorbent of visible light).

7.2.4 OTHER INSTRUMENTATION

A number of additional scientific instruments were operated during the MURFI field trial, all of which emulated a specific instrument that will be integrated onto ESA's ExoMars rover. The Aberystwyth University PanCam Emulator (AUPE) (J. K. Harris *et al.*, 2015) was able to simulate the ExoMars PanCam instrument (Griffiths *et al.*, 2006; Coates *et al.*, 2015). AUPE included a full array of filters and the High Resolution Camera (HRC) system (Cousins *et al.*, 2010). The AUPE instrument acquired daily images of the surrounding area, from which the SOT team were able to assess the geology and mineralogy of the region and select future science targets.



Figure 7.5: An image of the Starlight Xpress SuperHAD interline CCD detector system used in the MURFI field trials.

A digital single-lens reflex camera was used to simulate the ExoMars Close-up Imager (CLUPI) (Josset *et al.*, 2012). Once the science target was acquired the CLUPI emulator was used to specify regions of fine mudstone (avoiding hazardous sandstone material) from which drill cores could be acquired using a handheld drill system (analogous to the drill ExoMars will use to access 2m below the Martian surface). An ASD Inc. FieldSpec4

field reflectance spectrometer was used to simulate ExoMars' Infrared Spectrometer for Mars (ISEM) (Korablev *et al.*, 2013) and a handheld, miniaturised Raman spectrometer (using a 785nm laser) was used to analyse extracted drill samples.

Finally, the field instrumentation included a robotic instrument platform, which emulated the ExoMars rover skeleton (i.e. a robotic structure that was capable of traversing across the Utah terrain). The rover (shown in Figure 7.6) was a Q14 robot and included a four wheel steering drive, a passive dynamic suspension system and a range of motion and distance sensors (Balme *et al.*, 2017). The rover also encompassed a full mobile arm and a mast-mounted PanCam emulator which was used to acquire panoramic images.



Figure 7.6: A photograph of the Q14 rover platform provided by Oxford University. The PanCam emulator (also visible in the image) was mounted upon the mast.

7.2.5 FIELD RESULTS

Figure 7.7 (a) shows a close up of a typical calcite sample found at the mission site in Utah. Spectra were obtained from 5 randomly selected areas on the surface of the sample. Each time the sample was re-oriented, the probe head was realigned and clamped into an optimum position that refocused the laser light onto the surface. As described in Section 7.2.3, scattered light from the sample was collected by the instrument and distributed in the form of a spectral order on the system's CCD detector. Images were acquired using integration times of 120 seconds and with maximum laser power (i.e. 45mW). An example CCD image is shown in Figure 7.7(b).

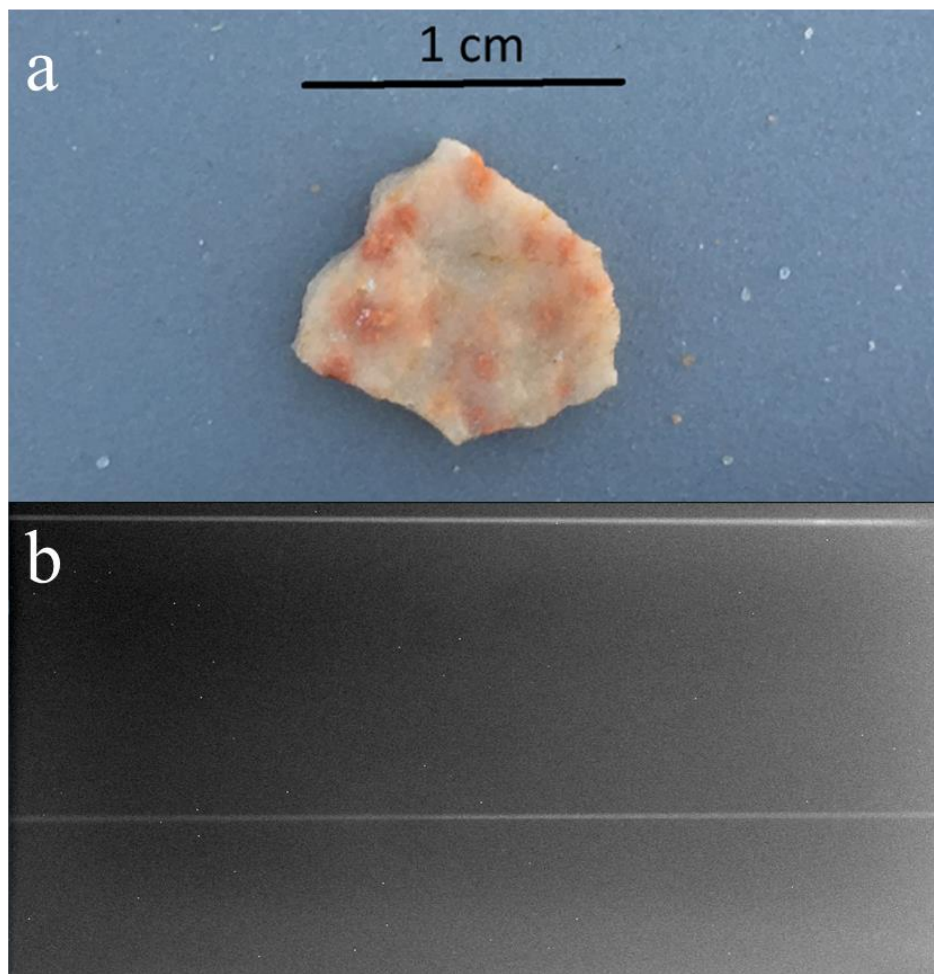


Figure 7.7: (a) A photograph of a typical calcite sample found in Utah. (b) An example CCD image containing the spectrum acquired from the MURFI sample.

The spectrograph distributes the collected light into two diffraction orders, both of which can be seen in Figure 7.7(b). The upper order contains a spectral feature towards the right of the image. The order subsequently begins to decrease in intensity towards the edge of the image as the respective wavelength approaches the range of the notch filter and the light is significantly attenuated.

The image also indicates that a significant amount of ambient light was incident on the detector during data acquisition. The background pixel intensity levels (pixels that do not contain charge generated by the diffraction order) increase across the image, indicating that the ambient light was directional and most likely caused by insufficient containment. Effects such as these can be reduced by subtracting a dark frame: a frame integrated for the same amount of time as a data frame (or a scaled down longer frame) but while there

is no signal present (in this case, with the laser not operating). The dark frame therefore contains the same level of background signal but does not include any Raman signal.

Raman spectra were extracted from the CCD image by appropriately summing the pixels containing signal from each of the diffraction orders. The resulting intensity is then plotted against pixel number. Each spectrum was subsequently calibrated using a spectrum of acetaminophen (obtained in the field using the same instrument configuration). The band positions in the acetaminophen spectrum are well known in wavenumber space, as well as pixel space, and can therefore be used to determine the conversion between pixel number and wavenumber.

7.2.6 PREDICTED INSTRUMENT PERFORMANCE

Using the CCD image in Figure 7.7(b), a number of expected SNR values have been derived for different instrument configurations using the model presented in Chapter 3. The predicted signal-to-noise ratios are summarised in Tables 2 and 3. The first column of the table shows the noise and signal values extracted from the data acquired during the field mission. The calcite band which occurs in the lower wavenumber range has an SNR value of ~52.

Table 7.2 shows that the SNR increases for an in situ Raman instrument by a factor of 2.5 when the instrument utilises a pulsed laser and a CCD42-10 cooled to -20°C. Even though the addition of a pulsed laser does increase the level of fluorescence (by a factor of 3.5) the dark current in the system is reduced by $68 \text{ e}^- \text{ s}^{-1}$ by sufficiently cooling a CCD42-10. The original dark current levels in the ICX205AL Sony SuperHAD were likely a result of the high ambient temperatures in the Utah desert and insufficient air flow within the unit containing the camera and spectrometer. Section 7.2.3 details the processes performed to minimise ambient light levels. However the ICX205AL Sony SuperHAD interline CCD camera used to acquire the data in the field required a low operating power and was cooled using air flow. The introduction of a TEC cooled CCD42-10 will increase operating voltage required to ~4.4V. This equates to a power of 7.92W when operated with a current of 1.8A. This is not unreasonable for terrestrial applications but may not meet field trial restrictions.

	Instrument Configurations				
	Measured	Simulated			
Configuration Number	1	2	3	4	5
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	9340.00	29187.50	29187.50	29187.50	29187.50
Fluorescence	10670.00	33343.75	33343.75	33343.75	0.00
Fluorescence Noise	103.30	182.60	182.60	182.60	0.00
Ambient Light	15324.00	15324.00	109.72	411.45	0.00
Ambient Noise	123.79	123.79	10.47	20.28	0.05
Dark Current	5494.00	30.12	110.18	0.81	43.50
Dark Noise	74.12	5.49	10.50	0.90	6.60
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	180.45	223.68	186.20	186.73	9.60
S/N	51.76	130.49	156.75	156.31	3041.64

Table 7.2: A summary of the SNR values calculated for four additional in situ instrument configurations based on the signal and noise levels in the original acquired data.

By operating the CCD42-10 in Shift Mode (1), the integrated ambient light level decreases by a factor of 140 from that observed in the original CCD image (obtained in the field). This implies that with no additional hardware changes, the ambient light levels detected by an instrument can be significantly decreased, readily improving the achieved SNR of a Raman instrument operating in daytime conditions. However, in this particular scenario, fluorescence emission continues to be the dominant source of noise (which is further increased when using a high powered pulsed laser), therefore the overall increase in SNR when using the pulsed readout mode was 1.2. Using the limited data acquired in the field, a full assessment of what is considered fluorescence signal was not possible (i.e. signal that is assumed to be fluorescence may be ambient light collected by the instrument's optical system). If this is the case then a fraction of what appears to be fluorescence signal (but is actually collected ambient light) will be removed during the shifting operation, as it will temporally separate from the relatively fast emission of fluorescence and Raman signal.

In terms of dark current, the first shifted operating mode generates a larger dark signal than the 'Static Stare' mode, due to the time taken to read out a row of charge from the CCD. However, the dark noise levels are still insignificant compared to the fluorescence levels. Alternatively, the dark current could be further reduced to a total of the $4.6e^-$ (for a 120second integration) by cooling the detector to -40°C . Overall, a Raman instrument using a pulsed laser and operating in Row Shift Mode (1) (Configuration 3) is expected to observe a calcite band with an SNR of ~ 157 when operating during daylight conditions.

The second row shifting mode, Shifting Mode (2), (Configuration 4) also significantly reduces the amount of ambient light acquired by the system. Compared to the 'Static Stare' operating mode, the ambient light level is reduced by a factor of 37. This operating mode is less effective than Shifting Mode (1) but allows for a reduction in dark current. When operating in row Shift Mode (2), the detector exhibits only $1.24e^-$ of dark signal after 120 seconds. Overall, this configuration enables the system to achieve an SNR of ~ 156 for a calcite band during daylight operation. By comparison with Configuration 3, Shifting Mode (2) offers significant ambient light reduction even if power requirements for the system prevent system cooling.

Configuration 5 uses a pulsed laser in conjunction with a gated detector. The model assumes that the use of a gated detector completely reduces the effects of fluorescence during data acquisition. Gated detectors such as the Princeton Instrument's PIMAX-4 electronically shutter the incident light on a 500 picosecond timescale. The short time scale of the acquisition window not only means that the system avoids the relatively delayed fluorescence but also that the window for ambient light collection is significantly reduced, while the amount of Raman signal collected remains unaffected (because it is collected over a large number of 7ns pulses). Since the field data indicated that fluorescence was the dominant source of noise, the theoretical SNR achieved by an instrument using a gated detector was the highest with a value of 3042 (as seen in Table 7.2). However, as described in Chapter 2, intensified CCDs perform the gating process using an oscillating high voltage which makes them challenging to qualify for some space applications. The photocathodes are also sensitive (and can be permanently damaged) by large signal levels (this damage is accelerated when the tube is gated on) and are more expensive and complicated than the alternative systems presented here.

Table 7.3 summarises the predicted SNR values for the calcite band, if it was observed by a stand-off Raman instrument operating at a distance of 4m. The introduction of a large stand-off distance decreases the Raman signal to 2% of that acquired in the field even with the incorporation of a telescope. The model suggests that by using ICX205AL Sony camera system operating in ‘Static Stare’ mode, the SNR for the calcite band will decrease to 0.02, which is not sufficient to enable a statistically significant detection.

	Instrument Configurations				
	Simulated				
Configuration Number	6	7	8	9	10
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	18.68	58.38	58.38	58.38	58.38
Fluorescence	21.34	66.69	66.69	66.69	0.00
Fluorescence Noise	4.62	8.17	8.17	8.17	0.00
Ambient Light	965412.00	965412.00	6912.35	25921.31	0.07
Ambient Noise	982.55	982.55	83.14	161.00	0.26
Dark Current	5494.00	30.12	110.18	0.81	43.50
Dark Noise	74.12	5.49	10.50	0.90	6.60
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	988.36	985.60	87.20	164.21	9.60
S/N	0.02	0.06	0.67	0.36	6.08

Table 7.3: A summary of the modelled SNR values expected to be achieved by stand-off Raman instruments operating at a distance of 4m.

The collected signal level is slightly increased (by a factor of 3.5) by utilising a pulsed laser. The incorporation of a CCD42-10 cooled to a temperature of -20°C decreases the estimated dark noise in the system. However in both static stare cases, the incorporation of a telescope’s optics significantly increases the amount of ambient light and is the dominant source of noise in this experimental scenario. Despite the reduced dark current levels, the SNR achieved for Configuration 7 is 0.06. This is also insufficient for a statistically significant detection of a Raman band.

Implementation of row Shift Mode (1) again decreases the ambient light level observed by the instrument by a factor of 140. However, at a distance of 4m, the Raman signal emitted by the calcite is still insufficient to increase the SNR of the configuration to above ~ 0.7 . Even though this is a significant increase in performance compared to Configurations 6 and 7, the SNR of the calcite band is not high enough to allow for spectrum statistically significant detection. Because the ambient light is the dominating source of noise in this situation, Shifting Mode (2) achieved an SNR of only 0.36. In this case the reduction of dark noise had little impact on instrument performance.

The use of a gated detector improves the SNR achieved by a stand-off system by up to a factor of ~ 6 . Compared to Row-Shifting Mode (1), the gated operation reduced the detected ambient light level by a factor of 620. In this particular experimental scenario, Configuration 10 is the only system likely to observe a calcite band from 4m in daylight operation.

It should be noted that this study did not take into account the effects of frame stacking or the impact that optimised data extraction techniques (i.e. extraction by summing of multiple pixels within a particular region of interest) have on the SNR values observed in acquired spectra. The typical effects that such process can have on spectral quality were discussed in Chapter 5, Section 5.2.5.

7.3 PLANETARY ANALOGUE MISSION 2: MINE ANALOGUE RESEARCH

7.3.1 MISSION OVERVIEW

The Mine Analogue Research (MINAR) mission was part of a research campaign lead by the UK centre for Astrobiology in collaboration with the Science and Technology Funding Council (STFC) that took place in Boulby Mine, the UK's only working potash and halite mine in Cleveland in northeast England. Boulby mine is part of the Israel Chemicals Ltd (ICL) group and specialises in mining sulphates and salt. The mine also hosts an underground dark matter laboratory (Boulby Underground Laboratory (Murphy and Paling, 2012)) and the Boulby International Subsurface Astrobiology laboratory (Cockell *et al.*, 2013), 1.1km below the Earth's surface (for the study of in situ sub-surface biology research and space technology development).

The overall MINAR mission consists of 6 scheduled campaigns, four of which have been completed since it started in 2012. The MINAR campaign has two aims: firstly to assess the geology and biochemistry of the extreme subsurface region to gain insight into potentially habitable environments elsewhere in the solar system (Payler *et al.*, 2017). This will be achieved using instrumentation designed for planetary surface exploration (in most cases analogous to instruments on current missions or due to be used on future missions, which are described in Section 7.3.4).

The second aim of the MINAR programme is to translate the technology and instrumentation developed for space exploration to the study and exploitation of extreme terrestrial environments, such as Boulby mine. The mining industry is faced with a number of challenges, many of which could be aided by the advances made by technology for planetary exploration. For ICL in particular, the challenges include: keeping a strong structural integrity throughout the mine (regardless of potentially hazardous material), the prevention of brine or water in-rushes and avoidance of flammable gas outbursts whilst locating and recovering mineral ores in an economic fashion (Bowler, 2013). Many of the techniques demonstrated during the MINAR missions may allow usually dangerous or inaccessible regions to be inspected prior to excavation (Payler *et al.* 2016).

Each campaign spanned two days, including over 10 hours at the experimental site within the mine (a location within the mine had been pre-selected based on its mineralogy and

accessibility). Once the suite of instruments had been set up and calibrated, three different sample sets were excavated from surrounding boulders and walls, each of which represented the array of minerals found in the mine. Each sample was catalogued and analysed by each of the instruments (listed in Section 7.3.4), in sequence.

7.3.2 SITE

Boulby Mine is situated in North Yorkshire, England, UK, as indicated in Figure 7.8 (a) and (b). Situated in the county of Cleveland (on the coast), the mine is between 0.8 and 1.1km deep, with 1,000 kilometers of tunnel under the North Sea (Talbot, Tully and Woods, 1982). The mine exploits an ancient evaporate deposit, formed in the waters of the Zechstien Sea; a body of water that covered North West Europe 250-260 million years ago.

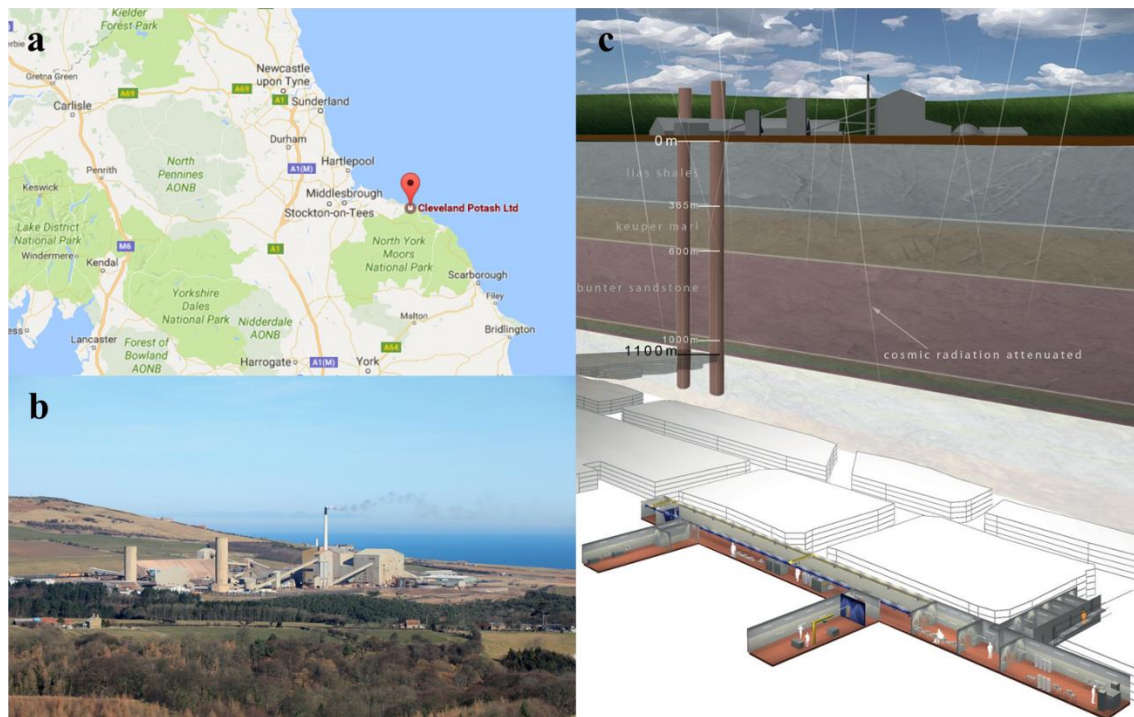


Figure 7.8: (a) shows the location of Cleveland Potash in the UK. Image (b) shows Boulby mine and the North Sea coast and (c) shows a schematic of the underground laboratories at a depth of 1.1km.

There are many aspects to Boulby mine that make it a suitable Mars or Lunar analogue site. In terms of mineralogy, the formation comprises chloride minerals, such as sylvinite (KCl), potash (also KCl) and halite (NaCl). Chloride minerals have been detected on the Martian surface from orbit (Osterloo *et al.*, 2008) and in Martian meteorite (Bridges *et al.*,

1999). The chloride minerals observed on the Martian surface differ only slightly from those found in the mine; the Martian chlorides are presumed to be more acidic and rich in iron, calcium, magnesium and silicon oxide (Tosca and McLennan, 2006).

The evaporate material also contains sulphate minerals including anhydrite (calcium sulphate) and gypsum (hydrated calcium sulphate). Much of the mined area also includes polyhalite, a triclinic potassium, calcium and magnesium sulphate (Cockell *et al.*, 2013). Similar materials, for example gypsum and jarosite, formed on the surface of Mars 3-3.5 billion years ago (Squyres *et al.*, 2004). On Earth, these minerals are often associated with the colonisation processes performed by extremophile organisms in sedimentary rocks (Edwards *et al.*, 2005).

Evaporate material may also play an important role in the preservation of biomarkers or potentially extant life on Mars. On Earth, microbes have been known to thrive in evaporated material from the Zechstien Sea (Dombrowski, 1963), above and below ground, and sulphate material in particular has been found to conserve bio-signatures. Aubrey *et al.* (2006) detected amino acids and their degraded products within sulphates such as gypsum and anhydrite. The evaporates found in Boulby mine have been found to contain various halophilic organisms within fluid inclusions in the sulphate material (Norton, McGenity and Grant, 1993).

In light of the upcoming ExoMars mission, many studies have concentrated on using Raman spectroscopy to identify and characterise organic molecules (such as carotenoids) in evaporated material analogous to those observed on the Martian surface or subsurface (Wynn-Williams, 2000; Marshall *et al.*, 2007; Vítek, Osterrothová and Jehlička, 2009; Vítek *et al.*, 2012; Jehlička and Oren, 2013). Carotenoids are coloured organic pigments produced by extremophiles, which allow them to survive and interact with the hypersaline environments. These molecules have indisputable biological origin (Marshall and Olcott Marshall, 2010) and in many organisms, they play an important role in UV radiation screening and DNA repair (Cockell *et al.*, 2008; Jehlička, Edwards and Oren, 2013). Culka *et al.* (2014) showed that instrumentation similar to that of the ExoMars RLS system (the RLS prototype located at the University of Leicester) could identify various carotenoids embedded within halite which was excavated from an evaporate pond in Eilat, Israel.

7.3.3 ADAPTED INSTRUMENTATION

In addition to the analogous mineralogy, Boulby mine offers an opportunity to deploy and test a Raman prototype system in a challenging environment, different to that experienced in Utah. The MINAR campaign took place in an alcove just off the main road way (the main tunnel stemming from the entrance of the mine) at a depth of 1.1km. The recess incorporated high walls and a ceiling (which provided areas of partial inaccessibility, ideally suited to testing stand-off Raman instrumentation in the future) and was naturally dark and warm, with ambient temperatures reaching at least 35°C (Abel and Djahanguiri, 1984). The immediate terrain was flat but covered in a fine layer of dust, with boulders of salt material distributed throughout the site.



Figure 7.9: A photograph of the tunnel in which the MINAR mission took place. During data acquisition periods, the white light source featured in the image was turned off to minimise ambient light levels. Credit: Mathew Gunn.

Similar to the system used in Utah, the Raman system was based on instrument Configuration 4, described in Chapter 3, Section 3.1.1. As well as being the smallest and most compact system, it is also the most analogous to the ExoMars RLS instrument.

The instrument excitation source was an Excelsior DPSS continuous wave laser which provided 80mW of power at 532nm. The laser was secured to an optical slab, along with an M-10X microscope objective (shown in Figure 3.7, Chapter 3, Section 3.1.2), which

was used to focus the laser light onto the end of an optical fibre. The alignment of this system was performed prior to field test campaign using a 1936-R Power Meter and a photodiode detector developed by Newport Corporation. The laser and its launcher were mounted in a lightweight container. The container prevented a build-up of dust and debris on the optical components (such as the detector and the spectrograph), which would otherwise reduce the amount of laser light incident on the sample and the efficiency with which the Raman emission is collected.

The laser light was focused onto a sample using a Kaiser Optical Systems MultiRxn Probe. Laser light entered through the top of the probe, via the fibre optic cable and was directed through a notch filter (which filters out light with wavelengths short or longer than 532nm). At the end of the probe, laser light was focused into a 0.5mm wide spot, 25.0mm from the end of the probe, by an 8.0mm wide exit compound lens. A full description of the probe head and its internal components is given in Chapter 3, Section 3.1.3.

The optical head and sample were located outside of the laser container but were also kept covered due to the close proximity of other instruments. Precautions were taken to minimise the amount of ambient light collected by the system.

Light scattered by the sample was collected by the same MultiRxn probe at an angle of 180° to the excitation source path. The collected light was filtered by the notch filter, which rejected most ($>99\%$) of the Rayleigh (elastically) scattered light. The filtered light was focused into a secondary optical fibre located towards the top of the probe head, parallel to the laser fibre.

The secondary fibre was coupled to a Kaiser Optical HoloSpec spectrograph, which comprised a collimating lens, a holographic diffraction grating and a moveable camera lens. Each of these components is described in full in Chapter 3, Section 3.1.4. The spectrometer had a large spectral range (175 cm^{-1} to 4400 cm^{-1} , distributed over two spectral orders) and was transportable as a single unit as each component was pre-aligned and fixed to a single optical plate. The spectrograph was also enclosed by an almost light-tight cover which not only reduced ambient light in the system but also minimised the accumulation of dust in the system.

The instrument's detector system was secured to the same optical slab and was positioned in front of the movable camera lens (see Figure 3.10 in Chapter 3). The detector system was aligned during set up (i.e. before the field test campaign in the mine). White light was directed through the instrument and used to gauge the optimum detector position that provided the greatest signal-to-noise ratio in each spectral order. The detector was a commercial off-the-shelf CCD system manufactured by Starlight Xpress. The system incorporated a ICX285AL Sony Exview interline CCD detector (a 8.98mm x 6.7mm device with a 1392 x 1040 array of pixels). Each pixel was 6.45µm in size and had a full well capacity of 40,000 e⁻. The detector quantum efficiency was ~65% at 540nm and the associated electronics provided ~8 e⁻ of read noise. The system was cooled by a two stage thermoelectric cooler which regulates the CCD to a temperature of -10°C. The system weighed approximately 350g and is encapsulated in a light-tight casing. The entire detector system required a 240V supply (at 750mA). Once aligned, the camera and spectrometer were installed in an enclosure (noting that the salt material can chemically degrade the system optics and electronics).

7.3.4 OTHER INSTRUMENTS

The MINAR mission was a large collaborative activity involving several institutions from the UK, each of which deployed instruments analogous to those developed for future planetary missions (such as ExoMars). For example,

- the University of Aberystwyth in collaboration with St. Andrews University, operated the PanCam emulator, AUPE-2. AUPE-2 was constructed from a selection of commercial, off-the-shelf cameras and lenses. The instrument included 22 filters (Cousins et al. 2012) and control software and was capable of obtaining context and spectral imagery with a field of view of 39° by 33° for the wide angle viewer and 4.8° by 4.8° for the high resolution imager (J. K. Harris *et al.*, 2015).

- As well as the Raman prototype instrument described in this chapter, the University of Leicester also deployed a second Raman instrument for comparative measurements. The DeltaNu, Inspector Raman instrument is a commercial, hand-held system that utilises a 785 nm excitation source exhibits a spectral range of 100 cm^{-1} to 2000 cm^{-1} and a spectral resolution of $< 8\text{ cm}^{-1}$. Figure 7.10 (a) and (b) show photographs of the instrument. The instrument was small and had a low mass (2.3 kg), making it ideal for the in situ field analysis of minerals.

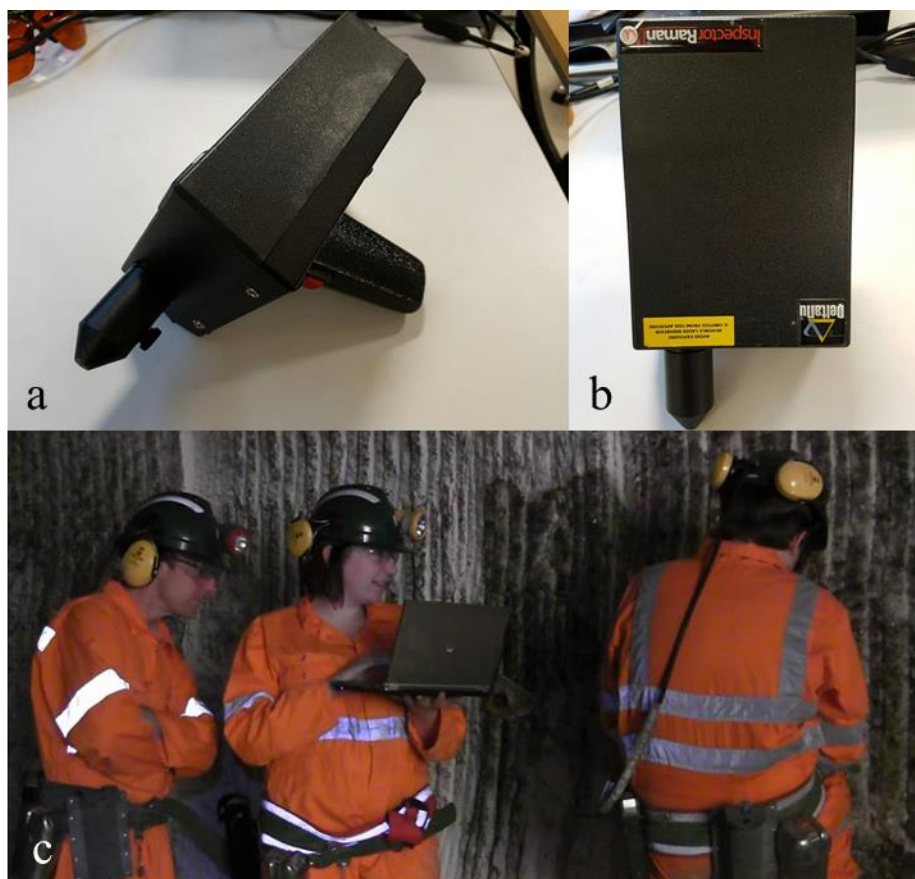


Figure 7.10: (a) and (b) are images of the hand-held commercial Inspector Raman instrument and (c) is a photograph of the team from the University of Leicester using the instrument to analyse material on the surface of the mine wall.

- An analogue to the Close-Up Imager on ExoMars (CLUPI) was provided by the Space Exploration Institute in Switzerland and was used to acquire sharp colour images of material at a distance of 10cm. The CLUPI emulator is very similar to the system developed for ExoMars (see Section 1.1.2 in Chapter 1). The instruments differ only in their collection optics (the emulator has a larger field of view). The instrument used calibration targets provided by Aberystwyth University and solar and UV lamps to illuminate the samples (Barnes *et al.*, 2014).

Samples were acquired from the subsurface using an Ultrasonic drill supplied by the University of Glasgow. The drill, which is a low power, low damage alternative to a rotational drill, uses a transducer to create small electrical pulses that are converted into small vibrations at a frequency of 20KHz. The vibrations excite a titanium horn tip which transfers a large amount of energy to the rock surface, pulverising it in the process (Xiaoqi Bao *et al.*, 2003).

- The final analytical instrument included on the MINAR mission was an XRD system, supplied by the University of Leicester (Hansford *et al.*, 2011). The instrument can perform rapid analysis of unprepared target samples. The instrument was used in a bench-top configuration to allow for multiple and extended acquisition times (Payler *et al.*, 2017).

7.3.5 FIELD RESULTS

In order to assess the overall performance of the instrument, several different types of sample were extracted from various regions within the experimental site (described in Section 7.3.2), representing the types of material found throughout Boulby Mine. These samples included minerals such as halite, sylvinite and polyhalite. Each sample was analysed in turn by the full array of instruments, including the Raman instruments described in this chapter. To obtain sufficiently high quality data, operating modes and acquisition parameters, such as integration times, number of acquisitions and laser power, were optimized for each individual sample. In most cases, spectra were acquired from multiple locations across the surface of a sample in order to investigate the heterogeneous distribution of material.

The following section presents a summary of the data collected by the prototype Raman instrument (detailed in Section 7.3.3), for two key samples. Each subsection gives a context image of the sample, a typical CCD image containing the spectral order produced by the analysed material, and an extracted Raman spectrum. The instrument performance is then discussed based on observed spectral features and signal-to-noise ratios.

SAMPLE 1

The first sample analysed during the MINAR field campaign was sylvinite; a synthesised mixture of sodium chloride (NaCl), potassium chloride (KCl) and calcium sulphate (CaSO_4). Figure 7. 11(a) shows a close up image of the surface of the sample (Sample 1). Spectra were obtained from 10 randomly selected areas on the surface of the sample. Each time the sample was reoriented, the probe head was realigned and clamped into an optimum position that refocused the laser light onto the surface. As described in Section 7.3.3, scattered light from the sample was collected by the instrument and distributed in the form of a spectral order onto the surface of the system's CCD detector. Images were acquired using acquisition times of 30-45 seconds and a maximum laser power of 45mW (measured at the sample). An example of an acquired CCD image is shown in Figure 7.11(b). The CCD image contains two diffraction orders, both containing spectral information from the sample. For example, at least three bands are visible in the upper

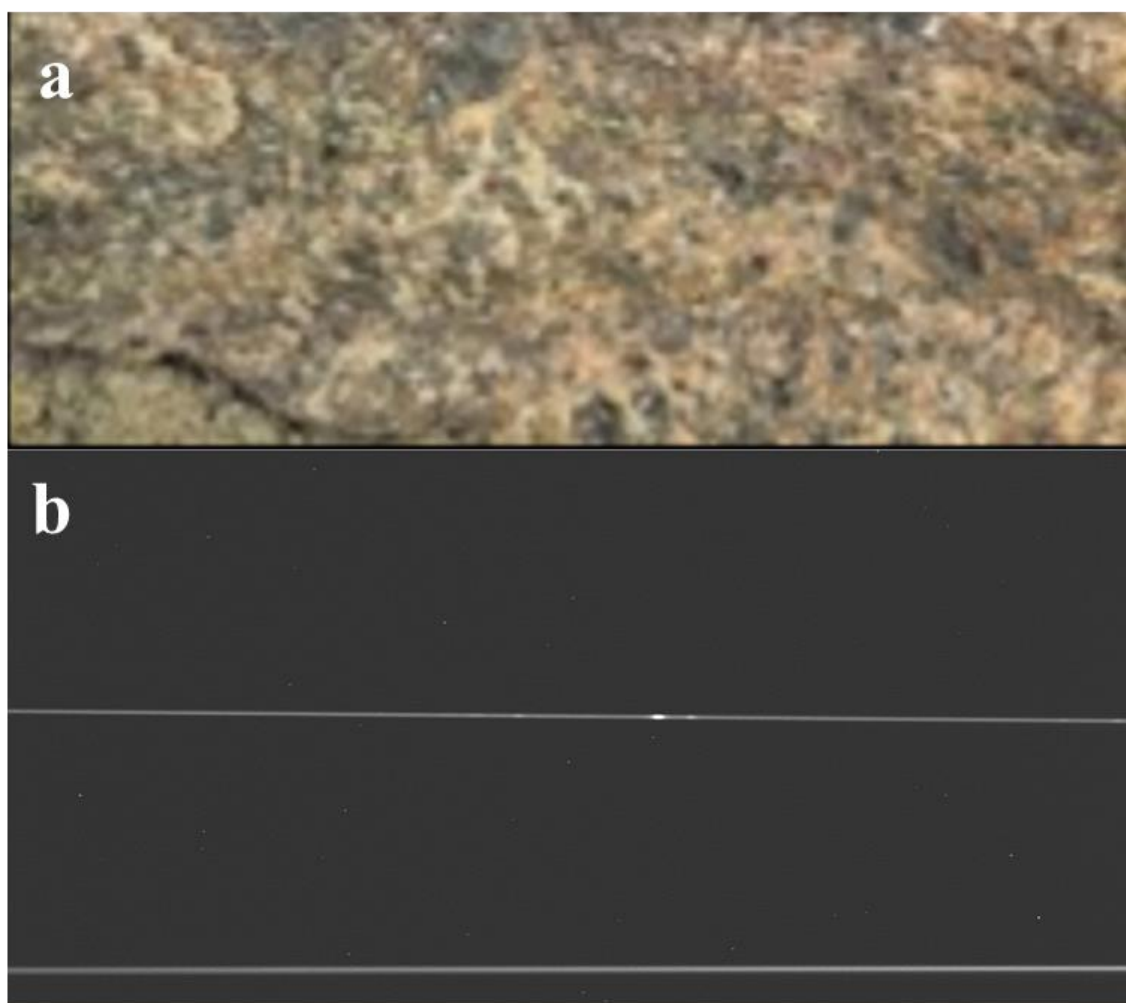


Figure 7.11: (a) A close up of the sample. The contrast in colour highlights the varying minerals present on the surface. (b) A typical CCD image acquired from Sample 1 using the prototype Raman instrument.

diffraction order shown in Figure 7.11(b). Raman spectra were extracted from the CCD image by appropriately summing pixels that contain signal from each diffraction order and plotting the resulting intensity as a function of pixel number.

Each spectrum was subsequently calibrated using a spectrum of acetaminophen that was obtained in the field using the same instrument configuration. A calibrated spectrum obtained from Sample 1 is shown in Figure 7.12.

The spectrum obtained from Sample 1 features several Raman bands that indicate the presence of gypsum, a hydrated CaSO_4 mineral. The strong band at 1009cm^{-1} results from the symmetrical stretching of the SO_4 (ν_1) anion. Bands at lower wavenumbers such as 620 cm^{-1} and 668 cm^{-1} are generated by anti-symmetric bending of the sulphate cation (ν_4) and the weak bands at 1122 cm^{-1} , 1136 cm^{-1} and 1153cm^{-1} are produced by antisymmetric stretch vibration modes (ν_3) (Liu, Wang and Freeman, 2009). The presence of water in gypsum can also be verified through the stretch vibration modes, typically evident in the 3000 cm^{-1} to 3500 cm^{-1} wavenumber range. Even though this instrument does have sufficient spectral capabilities to detect bands in this region, the camera configuration used during the trial limited the usable spectral range to 2000cm^{-1} and it

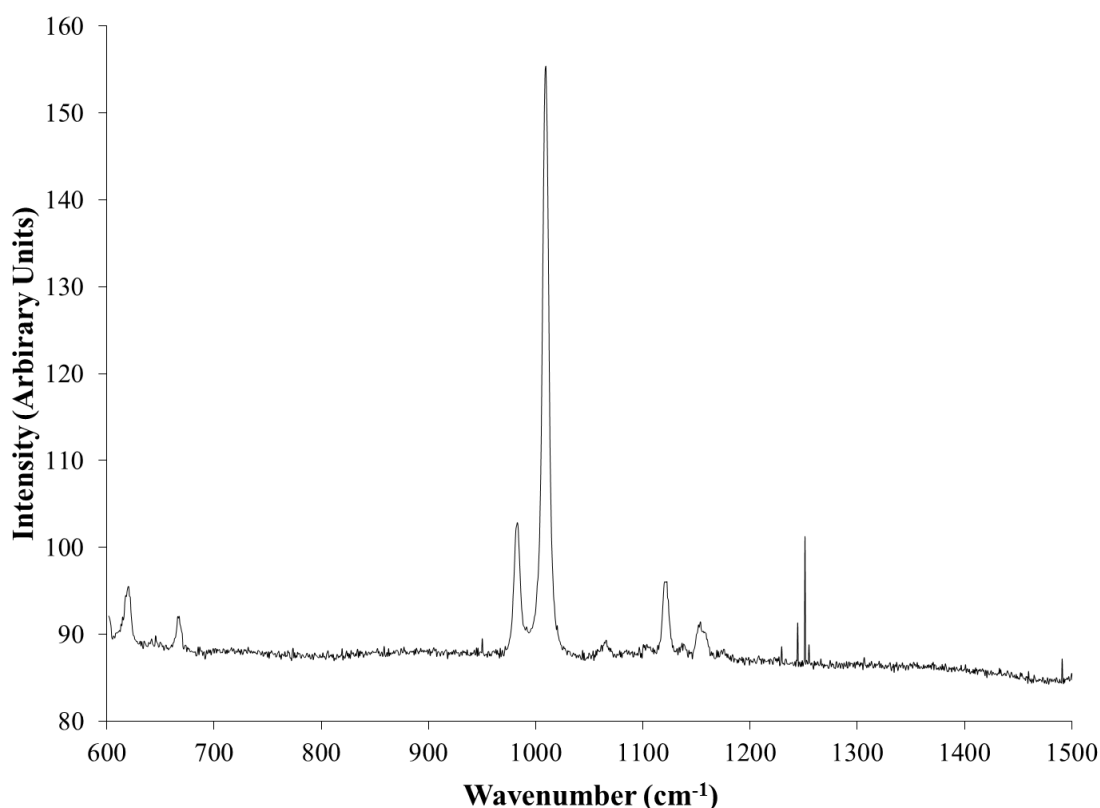


Figure 7.12: An example spectrum obtained from Sample 1 during the MINAR campaign.

was therefore not possible to observe the bands produced by water (Wang, Freeman, *et al.*, 2006). Similarly, the spectral bands associated with the lattice orders of NaCl and KCl (which exist as an ionic lattice structure) occur at much lower wavenumbers and are below the wavenumber limit of the instruments used in this study (Taurel, 1980).

The strong peak at 983cm^{-1} is also likely to result from the symmetrical stretching of an SO_4 anion. Mabrouk *et al.* (2013) show that the position of the ν_1 band shifts depending on the accompanying cation. In this case the position suggests the presence of a K_2 ion, which is not unexpected as the mine is known to contain a significant amount of polyhalite (which contains K_2SO_4 molecules). However a lack of corroborating bands leaves the identification of polyhalite ambiguous.

In addition to the Raman bands described above, at least three white (or hot) pixels are visible in the obtained spectra (i.e. at 1220 cm^{-1} , 1250 cm^{-1} and 1490 cm^{-1}). White pixels generate a higher level of dark current compared to neighbouring pixels and can sometimes be mistaken for spectral features (but can be readily removed from the spectra when the data are analysed appropriately). A pixel is typically considered to be a white pixel if it generates dark current ~ 100 times above the expected value for a pixel in the same detector at the same operating temperature. In Figure 7.12, the presence of white pixels are evident from the apparent large signal that is constrained to one or two consecutive pixels, unlike the visible Raman bands which span more than 5 cm^{-1} and ~ 10 consecutive pixels (due to the overall spectral resolution of each band).

SAMPLE 2

Figure 7.13 (a) shows a close up image of the surface of the second sample (Sample 2). This sample was analysed by acquiring 10 spectra from random areas on the surface of the sample. With each acquisition, the probe head was realigned and clamped into an optimum position that refocused the laser light onto the surface. The maximum laser power used was 45mW and spectra were acquired with 30-45 second integration times. Figure 7.13 (b) shows an example of a CCD image acquired when analysing the surface of the sample.

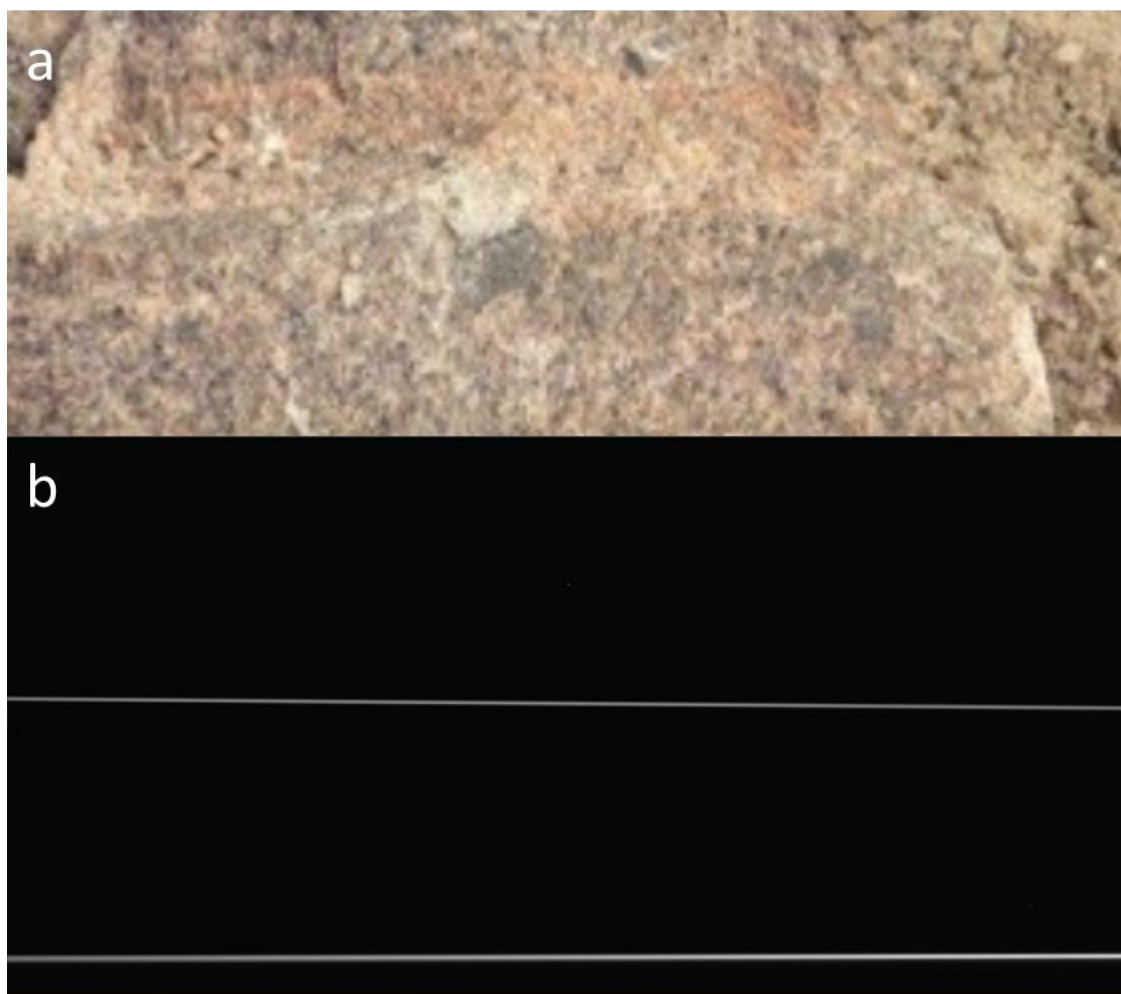


Figure 7. 13: (a) a close up image of the polyhalite sample analysed as part of the MINAR field mission. (b) A typical CCD image containing the acquired spectrum from the sample 2.

Both diffraction orders are clearly visible in Figure 7.13 (b), and the presence of Raman bands is apparent in both orders, above the fluorescence signal level. Spectra were extracted from the CCD images by appropriately summing pixels containing signal from each diffraction order and the resulting spectrum was then calibrated into wavenumber space using a spectrum of acetaminophen obtained in the field using the same instrument

configuration (as described above). Figure 7.14 shows a calibrated version of the spectrum obtained from Sample 2.

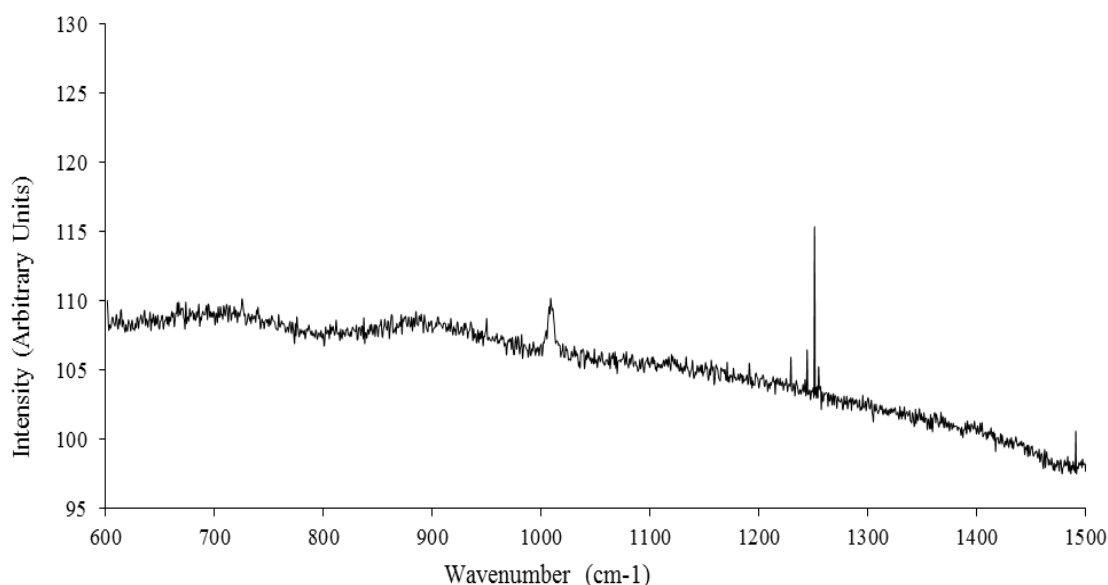


Figure 7.14: An example of a spectrum acquired from sample 2 during the MINAR campaign

In the spectrum only a single Raman band is apparent at 1014cm^{-1} . Given the intensity of the band above a large fluorescence background and the knowledge that the sample is known to contain polyhalite, the band is likely to be the symmetrical stretching mode of an SO_4 group within polyhalite. Given its centroid position (at 1014cm^{-1}), it is likely that it originates from the CaSO_4 group in polyhalite, since the ν_1 vibration modes of K_2SO_4 and MgSO_4 can be observed at 983cm^{-1} and 1021cm^{-1} respectively. It is also worth noting the presence of several hot pixels, which are significant compared to the weak signal collected from the sample. In spectra such as these, where the Raman bands do not have a high signal-to-noise ratio, hot pixels can have a large impact on the shape and intensity of spectral features.

7.3.6 PREDICTED INSTRUMENT PERFORMANCE

SAMPLE 1

To gain an understanding of the performance of the different Raman instruments when analysing these types of sample (i.e. such as Sample 1), the model described in Chapter 3 was used (in conjunction with the data acquired in the field) to estimate the SNR values that should be achieved using various configurations. The performance of these configurations were calculated for three different instrument scenarios in total: in situ analysis in a dark environment, in situ analysis in a medium level of ambient light and sample analysis at a stand-off distance of 4m in a medium ambient light level. These SNR values are summarised in Tables 7.4, 7.5 and 7.6 below.

	Instrument Configurations				
	Measured	Simulated			
Configuration number	1	2	3	4	5
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	8234.0	25731.3	25731.3	25731.3	25731.3
Fluorescence	4361.0	13628.1	13628.1	13628.1	0.0
Fluorescence Noise	66.0	116.7	116.7	116.7	0.0
Ambient Light	0.0	0.0	0.0	0.0	0.0
Ambient Noise	0.0	0.0	0.0	0.0	0.0
Dark Current	1881.0	11.3	41.3	0.3	16.3
Dark Noise	43.4	3.4	6.4	0.6	4.0
Read Noise	3.0	3.0	3.0	3.0	3.0
Total Noise	82.0	119.8	119.9	119.7	7.0
S/N	100.4	214.8	214.6	214.9	3655.5

Table 7.4: A summary of the theoretical SNR for the gypsum ν_1 band when analysed by various instrument configurations.

Table 7.4 summarises the estimated SNR values of the strong peak at 983cm^{-1} in Sample 1 when analysed by an in situ instrument in low level ambient light levels. The model

suggested that the SNR for the ν_1 vibration in gypsum improves by a factor of ~ 2 with the incorporation of a pulsed laser and a cooled CCD42-10 detector (Configuration 2 in Table 7.4). However, analogue field sites such as Boulby Mine, the ambient temperature can have a large impact on the detector dark current and therefore the achievable SNR.

Configuration 3 also incorporates a pulsed laser and CCD42-10 detector, but also operates in Row Shifting Mode (1) (see description in Section 7.1). No (or very little) ambient light was present during the acquisition of the data during the field mission, therefore the shifting technique has little impact in terms of improving the SNR achieved by the system in this scenario. The same reasoning can be applied to Configuration 4 which employs Shifting Mode (2). Operations such as these provide no performance enhancement when ambient light levels are low. However, this configuration exhibits the best performance while using the CCD42-10 but that is due to the minimised dark current achieved by the operating mode. All three additional configurations (2, 3 and 4) using a pulsed laser and a commercial device such as the CCD42-10 increase the SNR of the ν_1 band in gypsum by a factor of ~ 2.14 . The utilisation of a gated system increases the SNR by a factor of 17. This is a result of the reduced fluorescence signal acquired by the gated detector (discussed in detail in Section 7.2.6).

Table 7.5 summarises the performance of the first 5 in situ configurations in an ambient light environment. With the addition of ambient light, the SNR achieved by the in situ continuous laser system reduces to ~ 88 . The performance of an instrument using Configuration 2 (i.e. using pulsed laser and a cooled CCD42-10 operating in 'static stare' mode) is also reduced by ~ 13 due to the effects of ambient light.

Row shifting modes (1) and (2) reduce the ambient light to 22 e^- and 82 e^- from 3052 e^- respectively. Due to differences in operation, row shift mode (2) minimises the dark current to $< 1\text{ e}^-$ (over 45 seconds), compared to the 41 e^- generated by row Shifting Mode (1), resulting in an estimated SNR values of ~ 214 . These results suggest that the performance of Configurations 3 and 4 do not decrease due to the introduction of ambient light, unlike configuration 1 operating in 'Static Stare' mode.

In the same environment, the gated detector enables the instrument to reach a theoretical SNR of 3655. This is due to the very small window in which ambient light is able to fall on the detector. However as stated previously, the MCPs use intensified detectors that require a high voltage operation, which reduces their Technology Readiness Level (TRL).

For terrestrial applications the TRL of a device is less of an issue but if the samples provide a strong Raman signal and minimal amount of fluorescence, the shifted row mode options would be a less expensive alternative.

	Instrument Configurations				
	Measured	Simulated			
Configuration number	1	2	3	4	5
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	8234.0	25731.3	25731.3	25731.3	25731.3
Fluorescence	4361.0	13628.1	13628.1	13628.1	0.0
Fluorescence Noise	66.0	116.7	116.7	116.7	0.0
Ambient Light	2000.0	2000.0	14.3	53.7	0.0
Ambient Noise	44.7	44.7	3.8	7.3	0.0
Dark Current	1881.0	11.3	41.3	0.3	16.3
Dark Noise	43.4	3.4	6.4	0.6	4.0
Read Noise	3.0	3.0	3.0	3.0	3.0
Total Noise	93.8	128.1	120.0	120.0	7.0
S/N	87.8	200.9	214.5	214.5	3655.5

Table 7.5: A summary of the theoretical SNR for the gypsum ν_1 band when analysed by various instrument configurations in a medium ambient light level.

Table 7.6 contains the SNR values predicted for the ν_1 band in gypsum observed by stand-off Raman instrumentation. With the addition of a 4m working distance the SNR achieved by a system with a continuous laser is 0.05. This performance is therefore insufficient to enable statistically significant detection of signal above the background noise, even with the aid of a telescopic input system. In addition, the larger aperture size of the input optics, increases the amount of ambient light collected by the system.

Using a higher powered pulsed laser to excite Raman emission increases the SNR (at a distance of 4m) to a value of 0.14. A Raman band such as the ν_1 mode in gypsum would not be detectable at 4m by stand-off Raman system utilising a 'static stare' mode of operation.

The performance is increased further (by a factor of ~ 10) when operating the CCD42-10 in Row Shifting Mode (1). The ambient light level is again reduced by a factor of ~ 140 , however, the weaker signal at a distance of 4m reduces the SNR value achieved. Shifting Mode (2) improves the performance by a factor of 6 compared to the 'static stare' pulsed laser system of Configuration 6 but the performance of the system is still limited by the weak Raman signal detected by the instrument. Because of this, neither shifting mode would produce a sufficient SNR that would allow the gypsum ν_1 band to be detected.

	Instrument Configurations				
	Simulated				
Configuration number	6	7	8	9	10
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	16.47	51.46	51.46	51.46	51.46
Fluorescence	8.72	27.26	27.26	27.26	0.00
Fluorescence Noise	2.95	5.22	5.22	5.22	0.00
Ambient In Diffraction Order	126000	126000	902.16	3383.10	0.01
Ambient Noise	354.96	354.96	30.04	58.16	0.09
Dark Current	1881.00	11.33	41.32	0.30	16.31
Dark Noise	43.37	3.37	6.43	0.55	4.04
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	360.62	358.02	34.16	61.40	7.04
S/N	0.05	0.14	1.51	0.84	7.31

Table 7.6: A summary of the theoretical SNR for the gypsum ν_1 band when analysed by various stand-off instrument configurations in a medium ambient light level at a distance of 4m from the sample.

The integration of a gated camera theoretically improves the system performance by a factor of 5 compared to Row Shifting Mode (1), allowing for the likely detection of the ν_1 band observed in Figure 7.14. However, the weaker bands observed in the spectrum obtained from Sample 1 would not be detectable using this system, due to the limited signal collected at a distance of 4m.

SAMPLE 2

To fully investigate the limits of the theoretical configurations and operating modes, the software model was also used to derive SNR values for the weak band observed in Figure 7.14 (a Raman spectrum acquired from Sample 2). In a manner similar to that described in Section 7.3.6, SNR values were calculated for three different instrument scenarios: in situ analysis in a dark environment, in situ analysis in a medium level of ambient light and sample analysis at a stand-off distance of 4m in a medium level of ambient light. These SNR values are summarised in Tables 7.7, 7.8 and 7.9.

	Instrument Configurations				
	Measured	Simulated			
Configuration number	1	2	3	4	5
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	767.00	2396.88	2396.88	2396.88	2396.88
Fluorescence	5501.00	17190.63	17190.63	17190.63	0.00
Fluorescence Noise	74.17	131.11	131.11	131.11	0.00
Ambient Light	0.00	0.00	0.00	0.00	0.00
Ambient Noise	0.00	0.00	0.00	0.00	0.00
Dark Current	1818.00	11.33	41.32	0.30	16.31
Dark Noise	42.64	3.37	6.43	0.55	4.04
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	88.55	134.16	134.27	134.11	7.04
S/N	8.66	17.87	17.85	17.87	340.51

Table 7.7: A summary of the theoretical SNR for the singular band visible in Figure 7.14 when analysed by various in situ instrument configurations. The first column (configuration 1) contains the signal and noise break down extracted from Figure 7.14

Table 7.7 summarises the estimated SNR values of the suspected CaSO_4 ν_1 band in Sample 2 when analysed by an in situ instrument in low level ambient light levels. The model shows that the SNR for the band in Sample 2 improves by a factor of 2 when using an instrument setup such as Configuration 2, i.e. an instrument that incorporates a more powerful pulsed laser and CCD42-10 detector cooled to -20°C .

Configurations 3 and 4 also use a pulsed laser but operate the CCD42-10 in Row Shifting modes (1) and (2) respectively (see Section 7.1). Since the data presented in Section 7.3.5 were acquired in an environment with very little ambient light, the implementation of shifting modes does not improve the SNR achieved by the system in this particular scenario. The small difference in SNR achieved by Row Shifted mode (1) and (2) is a result of the dark noise generated during the operation since charge is shifted through a larger number of rows within the device during Row Shifted Mode (1). Because of the lack of ambient light, Configurations 2, 3 and 4 (that use a pulsed laser and a CCD42-10 device) achieve an SNR of 17.8 for the sample 2 band. The integration of a gated camera into the system further increases the SNR by a factor of 19. This is a result of the reduced fluorescence signal acquired by the gated detector (discussed in detail in Section 7.2.6).

	Instrument Configurations				
	Measured	Simulated			
Configuration number	1	2	3	4	5
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	767.00	2396.88	2396.88	2396.88	2396.88
Fluorescence	5501.00	17190.63	17190.63	17190.63	0.00
Fluorescence Noise	74.17	131.11	131.11	131.11	0.00
Ambient Light	2000.00	2000.00	14.32	53.70	0.00
Ambient Noise	44.72	44.72	3.78	7.33	0.01
Dark Current	1818.00	11.33	41.32	0.30	16.31
Dark Noise	42.64	3.37	6.43	0.55	4.04
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	99.53	141.57	134.33	134.32	7.04
S/N	7.71	16.93	17.84	17.84	340.51

Table 7.8: A summary of the theoretical SNR achieved by various in situ instrument configurations for the singular band visible in Figure 7.14, in medium ambient light conditions.

In order to fully understand in situ instrument performance in all environments, the first 5 configurations were also simulated assuming a medium level of ambient light. The results obtained from these simulations are shown in Table 7.8. The addition of ambient light reduced the SNR achieved by the in situ continuous laser system to ~ 1 . For Configuration 2, the increase in laser power increased the Raman signal (and fluorescence

emission). However the use of a cooled CCD42-10 operating in 'static stare' mode meant that the additional ambient light only reduced the SNR by ~ 1 .

Configuration 3 implements Row Shifting Mode (1) in order to reduce the amount of ambient light integrated by the CCD. The model indicates that in an experimental scenario where the ambient light level is $\sim 25\%$ that of the Raman signal, Row Shifting Mode (1) will improve the instrument performance by a factor of 2.3. Similar to the simulation presented in the Sample 1 section. Row Shifting Mode (1) reduces the level of ambient light detected by the system slightly more than Shifting Mode (2). However Rows Shifting Mode (2) generates 137 times less dark current than shifting mode (1), meaning their respective estimated SNR are still ~ 17.8 for the band observed in Sample 2. Once again, the performance of Configurations 3 and 4 does not decrease due to the introduction of ambient light, suggesting that row shifting modes are an effective method of reducing ambient light in Raman spectra. The final configuration (Configuration 5) uses a gated detector which enables the instrument to reach a theoretical SNR of 340. This is largely as a result of the absence of a fluorescence signal in the acquired data.

Table 7.9 contains the SNR values predicted for the potential CaSO_4 band observed by stand-off Raman instrument. With the addition of a 4m working distance the SNR achieved by a system with a continuous laser has decreased to less than 0.01. Despite the integration of a telescope into the collection optics, this performance of the system is no longer sufficient to detect signal above the noise levels. Table 7.9 shows that the decrease. In addition, the larger aperture size of the input optics, increases the amount of ambient light collected by the system. By incorporating a more powerful pulsed laser and a cooled CCD42-10, the SNR (at a distance of 4m) increases to a value of 0.01 (from 0.0). However, the band would still not be detectable above the observed noise level.

When operating the CCD42-10 in Row Shifting Mode (1), the performance of the stand-off instrument is increased by a factor of ~ 10 . The ambient light level is again reduced by a factor of ~ 140 . However, the weaker signal at a distance of 4m reduces the SNR values that can be achieved. Row Shifting Mode (2) improves the performance (by a factor of 6 compared to configuration 1) but the system is still limited by the weak Raman signal detected by the instrument. As result, Configurations 3 and 4 would not produce a sufficient SNR to enable the band to be detected with sufficient statistical significance.

In previous simulations, the integration of a gated camera theoretically increases the SNR value above the detection limit (assuming it is twice as large as the noise). However, the low Raman signal acquired from the sample at a distance of 4m results in an SNR of only 0.68 for the gated system. In this scenario, the signal was too weak to be detected against the dark current level generated by the detector (which is relatively low).

	Instrument Configurations				
	Simulated				
	6	7	8	9	10
Signals and Associated noise (ADU)	Continuous Non gated	Pulsed Non gated	Pulsed Shifted (1)	Pulsed Shifted (2)	Pulsed Gated
Raman Signal	1.53	4.79	4.79	4.79	4.79
Fluorescence	11.00	34.38	34.38	34.38	0.00
Fluorescence Noise	3.32	5.86	5.86	5.86	0.00
Ambient Light	126000.00	126000.00	902.16	3383.10	0.01
Ambient Noise	354.96	354.96	30.04	58.16	0.09
Dark Current	1818.00	11.33	41.32	0.30	16.31
Dark Noise	42.64	3.37	6.43	0.55	4.04
Read Noise	3.00	3.00	3.00	3.00	3.00
Total Noise	360.53	358.03	34.27	61.46	7.04
S/N	0.00	0.01	0.14	0.08	0.68

Table 7.9: A summary of the theoretical SNR for the gypsum v1 band when analysed by various stand-off instrument configurations in a medium ambient light level at a distance of 4m from the sample.

7.4 SUMMARY

This chapter describes the deployment of an in situ Raman instrument in two challenging field locations. The data collected during the field campaigns provided a basis to evaluate and model the performance of alternative Raman systems in environments that exhibit high ambient temperatures and varying levels of ambient light. This chapter gives details on the two field campaigns (the Mars Utah Robotic Field Investigation and the Mine Analogue Research mission) and describes the campaign aims, sites and their geological

and mineralogical relevance to planetary exploration. The planetary analogue locations not only provided harsh test environments but also provided an opportunity to test and model the instrumentation using real, unprepared samples.

Spectra that were acquired in the field were used to model the performance of different Raman instrument configurations. These configurations included the use of either a continuous laser or a pulsed laser. In each scenario the model suggested that the integration of a pulsed laser increased the Raman signal (and fluorescence emission) from a field sample. However the model assumed that the incident power from the laser was still below the damage threshold of the material. The model also simulated the effects of operating over different working distances (i.e. in situ and stand-off systems). The extended distance between the sample and instrument decreased the amount of signal collected by the instrument. However, the effects were mitigated slightly by the incorporation of telescopic input optics.

In addition, the model was used to compare the performance of a system that used a commercial off the shelf camera package (with limited cooling capability) and a commercial CCD system that was cooled to a temperature of -20°C . The cooled commercial CCD system generated minimal dark current and therefore increased the system performance.

The model was also used to simulate the commercial CCD operating in a standard ‘Static stare’ mode and two continuous row shifting modes, as well as a system that utilises a gated, intensified detector system. Although (according to the model) the use of a gated system achieves the best performance in each scenario, the model showed that the continuous Row Shifting Modes are able to prevent significant performance degradation in medium ambient light conditions (compared to an identical system operating in darkness or a ‘static stare’ operating mode), suggesting that these modes are a straightforward, software-based method of reducing the effects of ambient light. Often stand-off Raman systems use gating techniques that rely on additional hardware (which does not necessarily have a high TRL) to achieve a high signal-to-noise ratio. Operating modes such as these will be essential for optimising systems such as stand-off Raman instruments for high ambient light environments, such as during daytime operations on Mars or the Moon and during terrestrial applications where it is not possible to exclude ambient light

CONCLUSIONS

In the year 2020, both ESA and NASA will launch analytical payloads towards the surface of Mars in the form of planetary rovers (ExoMars and Mars2020 respectively). Both rover payloads will incorporate Raman spectrometers. In the case of ExoMars, this will be the Raman Laser Spectrometer (RLS) instrument; a Spanish led instrument developed in collaboration with France, the UK (the University of Leicester and the Rutherford Appleton Laboratories) and Germany. The RLS is a miniaturised, robust and mature Raman instrument that will analyse material beneath the surface (utilising the rover's 2m drill). The NASA Mars 2020 mission will deploy a stand-off Raman spectrometer, which will provide mineralogical information from a remote distance, enabling the rover to access regions of interest (that might normally be inaccessible) without the need to relocate and use limited rover resources.

Currently Raman instrument designs are limited by the challenging mass, power and data rate constraints associated with planetary rover missions. The stand-off Raman technique then provides further challenges as additional hardware and complex operating modes are required to not only maximise the amount of Raman signal collected by the instrument but to minimise the impact of the various sources of background noise. In the case of stand-off Raman spectroscopy, telescopic optics, pulsed lasers and rapid detector operation are required to obtain spectra from a remote distance and to reduce the impact of ambient light, sample fluorescence and detector dark current. The many inter-relating parameters and complicated trade-offs that arise in the development of such complex instruments can be investigated using a radiometric model. Radiometric models provide a method of understanding the performance of each aspect of a stand-off or in situ Raman system and can be used as a tool to assess and optimise the overall capability of a system. Models such as these are essential to fully understand the overall performance of Raman systems given the constraints imposed by the demanding environment, mission engineering constraints and the mission science objectives.

The work presented in this thesis focuses on the development of a software model in preparation for not only ExoMars and Mars2020, but also future planetary missions to the Moon and Venus. Chapter 1 described the history of robotic exploration of Mars, Venus, the moon, Europa and Titan and gave provided overviews of the key scientific findings and technical challenges associated with each mission, including how they have informed

more recent and current exploration missions. Descriptions of future mission plans and the scientific aims of those missions mission (including potential strawman payloads that could meet those requirements) are also provided.

Chapter 2 provides an overview of the current technology being used to develop Raman instrumentation for space exploration, including excitation sources, output optics, input optics, spectrographs and detectors. The options available and how their performance characteristics impact on the overall performance of the system are discussed in detail.

In light of future mission (scientific and engineering) requirements, Chapter 3 describes the development and build of a stand-off Raman spectrometer. The instrument was developed as a proto-type for future mission opportunities and was also used to test and verify the software simulation models. Consequently, the system was specifically designed to be flexible and adjustable so that it could adopt multiple configurations (in order to verify the full range of radiometric parameters) and provide in situ measurements as well as obtain stand-off data. The chapter gives details on each instrument subsystem and how they vary in each configuration.

The chapter describes the set of algorithms used to produce the radiometric model and to model the end-to-end performance of each subsystem and the instrument as a whole. It then describes how the simulator can be used to estimate and optimise instrument performance.

Chapter 4 describes the system simulator: a Monte Carlo based simulation (that incorporates the algorithms detailed in Chapter 3) which provides a method of exploring the many parameters that impact on the performance of the instrument including low level detector operations and the effects of radiation damage. The chapter then provides details on how the simulator can inform system optimisation and how it can be used to provide instrument design recommendations for instruments in challenging operating environments.

Chapter 5 describes the software interface that was developed as a tool to optimise instrument data acquisition strategies, provide control of supporting hardware systems and thermal interfaces and optimise instrument performance in real time. The chapter also describes a set of throughput measurements acquired to verify the capability of the radiometric model and the performance of each subsystem.

Results from two Raman spectroscopy studies that were performed to assess the overall scientific performance of the instrument are also presented. The first study analysed a terrestrial halite sample containing different carotenoids using a prototype of the ExoMars RLS instrument in order to assess the capability of the instrument with particular emphasis on the impact of spectral resolution. The study demonstrated that with a spectral resolution of $\sim 3\text{cm}^{-1}$, it was possible to sufficiently discern between subtly different carotenoids that key scientific conclusions could be made about the samples under test (which were directly relevant to the science goals of future planetary exploration missions).

The second study demonstrated the performance of the proto-type stand-off instrument developed in this thesis (described in Chapter 3) and verifies the performance benefits of using processes such as frame stacking and detector intensifiers.

Two more spectroscopy studies are detailed in Chapter 6, both of which demonstrate the performance of flight-representative Raman instruments. The first study uses the Compact Integrated Raman Spectrometer (CIRS) instrument developed by Washington University, USA, the Jet Propulsion Laboratory and the University of Leicester. The instrument was used to obtain spectra from a range of mission relevant minerals in order to assess performance and mineral detection limits and outputs from the simulator were used to optimise the design and operation of the camera system and the operation of the instrument as a whole.

The second study used the Raman Laser Spectrometer (RLS) Simulator and the Sample Preparation and Distribution System (SPDS) emulator to replicate the ExoMars mission sample analysis sequence and analyse an analogue of a carbon bearing meteorite sample. Through the measurement of spectral band characteristics of thermally altered carbon, the study showed that the ExoMars instrument will be able to discern non-thermally altered material and results from the simulator modelling provide insight into how to optimise the operation of the instrument for such measurements.

Finally, Chapter 7 provides detailed descriptions of two field campaigns in which the performance of a flight prototype Raman instrument was tested and characterised in non-laboratory environments. Both missions took place in difficult environments and provided samples of mineralogical relevance to Mars mission preparations. A series of Raman spectra acquired from a range of analogue samples identified at each site are

presented. The spectra acquired during the field test campaigns were then used in conjunction with the radiometric model described in Chapter 3, to simulate the performance of 5 specific instrument configurations (operating in various conditions) when acquiring spectra from samples similar to those found in the field locations and operating in similar environmental conditions. It was verified that the stand-off instrumentation described in previous chapters would be able to perform sufficiently, acquiring data that would allow mineral identification, assuming certain operating modes (such as the shifting mode) or hardware alterations (such as the integration of light-tight enclosures and structural supports for optical components) could be made to increase the robustness of the instrument.

FURTHER WORK

The continued development of the simulator will focus on adding other analytical techniques to the system, such as LIBS or infra-red spectroscopy. The model could then be used to investigate how multiple techniques could be combined into a single instrument in order to provide chemical, molecular and mineralogical capability. In addition further development of the model would enable mission-specific studies to be performed so that recommendations could be made regarding specific configurations and operating modes. For example, using the simulator to develop an instrument that could perform adequately over distances of up to 10m during day light conditions (and with a scanning mechanism in order to characterise an area of interest on the planetary surface).

Further work on prototype instrument design would include evaluating the relationship between the laser wavelength and the thermal stability, which would define the impact that laser wavelength shifts would have on the detectability of Raman band positions and completing sample characterisation tests for both the ESA ExoMars RLS instrument and the NASA JPL CIRS instrument.

The spectroscopic studies presented in Chapters 5, 6 and 7 demonstrate the importance of using natural analogue samples to assess instrument performance. Further work would include not only extending the range of samples to more complex materials but would also include replicating the studies using a stand-off Raman instrument to assess the limitations of a potential reconnaissance instrument on natural analogue samples. This

test would also provide a method of evaluating which instrument configurations and operating modes are best suited to specific materials and therefore mission objectives.

The spectroscopic studies will also be extended in a number of other ways. For example, the study described in Chapter 5 used sulphur as a standard sample, however it is important to consider other mission relevant materials, such as carbonates and sulphates (e.g. calcite and gypsum), to fully assess the full capability of an instrument in a mission scenario.

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