

DEPARTMENT OF PHYSICS AND ASTRONOMY

Radio and Space Plasma Physics Group

The Search for Life: Development of an Analytical Camera System for Space Applications.

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Under the supervision of Dr 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

Since the first detailed observations made by the Voyager probe, Jupiter's moon Europa has been a key target for astrobiological exploration. Previous missions have provided evidence of a subsurface ocean, source of internal heating and geological activity. This evidence, with recent developments in instrument technology, has resulted in space agencies focusing their efforts on the exploration of Europa.

The next generation of landers will aim to assess Europa's habitability and capacity to support life using analytical instruments (e.g. Raman and UV-Vis fluorescence spectrometers). To achieve the science goals of the mission, these instruments will be required to operate effectively in extreme temperature and radiation conditions. In preparation for Europa lander missions, this thesis presents the development of a multi-analytical technique camera system suitable for operation on Europa. It describes the current CCD and CMOS detector systems, outlines key performance characteristics, how they address science requirements of future missions, and highlights challenges associated with harsh environments. It presents the use of a Monte Carlo simulation replicating spectral output of a detector system in extreme radiation conditions to predict, evaluate and optimise system performance. Details of proton irradiation campaigns are provided, along with analysis of the resulting camera performance. Suggestions are given for design, architecture and operating modes to ensure reliable data acquisition capable of achieving mission goals. Using analytical spectroscopy studies, instrument sensitivity levels were assessed using Europan analogue samples. Spectra acquired during a field campaign to a planetary analogue site and data acquired using existing flight instrument (ExoMars) prototypes are presented and used to assess performance of systems in a Europa-like environment.

Outlined are the need for combined analytical techniques when considering mission science goals and strict engineering requirements, the development of a novel quadrant detector system capable of performing Raman, UV fluorescence and X-ray fluorescence spectroscopy and context imaging.

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List of Acronyms and Abbreviations

AFM	Atomic Force Microscope
AIMO	Asymmetric Inverted Mode Operation
ALD	Analytical Laboratory Drawer
APS	Active Pixel Sensor
APXS	Alpha Particle X-ray Spectrometer
AR	Anti-Reflection
CAPS	Cassini Plasma Spectrometer
CCD	Charged-Couple Device
CDA	Cosmic Dust Analyzer
CDS	Correlated Double Sampling
CIRS (Cas)	Composite InfraRed Spectrometer on Cassini
CIRS	Compact Integrated Raman Spectrometer
СМ	Carbonaceous Mighei
CMOS	Complementary Metal-Oxide-Semiconductor
CSA	Canadian Space Agency
СТЕ	Charge Transfer Efficiency
СТІ	Charge Transfer Inefficiency
DC	Dark Current
DR	Dynamic Range
DSNU	Dark Signal Non-Uniformity
DWARF	Dual WAvelength Raman/Fluorescence
EJSM	Europa Jupiter System Missions
ESA	European Space Agency

FET	Field Effect Transistor
FPGA	Field Programmable Gate Array
FPN	Fixed Pattern Noise
FWC	Full Well Capacity
GIRE	Galileo Interim Electron Environment
ICE	Instrument Control Environment
IMO	Inverted Mode Operation
INMS	Ion and Neutral Mass Spectrometer
іОН	Optical Head unit
IR	InfraRed
ISM	Infrared mapping SpectroMeter
ISS	Imaging Science Subsystem
JAXA	Japanese Aerospace eXploration Agency
JEO	Jupiter Europa Orbiter
JGO	Jupiter Ganymede Orbiter
JPL	Jet Propulsion Laboratory
JUICE	JUpiter ICy moon Explorer
LED	Light Emitting Diode
LIF	Laser Induced Fluorescence
LSB	Least Significant Bit
MAG	MAGnetometer
MER	Mars Exploration Rover
MMRS	Mars Microbeam Raman Spectrometer
ММХ	Mars Moon eXploration
MOS	Metal-Oxide-Semiconductor
MRO	Mars Reconnaissance Orbiter

MTF	Modulation Transfer Function
NASA	National Aeronautics and Space Administration
NIMO	Non-Inverted Mode Operation
NIMS	Near-Infrared Mapping Spectrometer
NIR	Near-InfraRed
NRC	National Research Council
PR	Photon Rate
PTC	Photon Transfer Curve
PRNU	Pixel Response Non-Uniformity
PRT	Platinum Resistance Thermometer
QE	Quantum Efficiency
RLS	Raman Laser Spectrometer
RMS	Root Mean Square
ROI	Region Of Interest
RPWS	Radio and Plasma Wave Science instrument
RTI	Radiation Trap Inefficiency
RTS	Random Telegraph Signal
SERDS	Shifted Excitation Raman Difference Spectroscopy
SHERLOC	Scanning Habitable Environments with Raman and Luminescence
SNR	Signal-to-Noise Ratio
SPU	SPectrometer Unit
SSES	Sequential Shifted Excitation Spectroscopy
TEC	ThermoElectric Cooler
TGO	Trace Gas Orbiter

TRL	Technology Readiness Level
UV	UltraViolet
UVIS	UltraViolet Imaging Spectrograph
VIMS	Visual and Infrared Mapping Spectrometer
VIS	VISible (light)
VSK	Videospectrometric System
XRF	X-Ray Fluorescence

List of Publications

This section outlines the publications that I have written or contributed to during the PhD.

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Chapter 1 The Search for Life

It was only 200,000 years ago when our ancestors, the early humans, diverged from other primates along the final path of the evolutionary tree into the humans living on Earth today. However, humans have been on this planet for a relatively small amount of time compared to the length of time life has inhabited the Earth. Other mammals have been living for up to 220 million years prior to the modern day; Tetrapoda (four limbed vertebrates) for 395 million years; Animalia (any multicellular eukaryotic organism) for 590 million years; and Eukaryota (any cell with a nucleus) since 2,100 million years ago (Roger & Simpson 2009).

But where did the cells originate and why did they come into origin 2,100 million years ago? What caused them to begin the evolution into the number of species occupying the planet today? Importantly, can this process have occurred anywhere else in the universe?

Whilst searching for life elsewhere in the universe it is vital to acknowledge that life may have been present or may evolve on a body in the future, if the environment can support such processes. To determine how likely it is that the planet or moon can support life either in the past or future, it is necessary to define the habitability of the planet or moon, that is, the ability to support the processes and evolution of life. As stated in Cockell et al. (2016), one possible definition of habitable in the search for life is "an environment capable of supporting the activity of at least one known organism," where "activity" is metabolic activity allowing for survival, maintenance, growth, and/or reproduction. It is important to note that the current search for life explicitly looks for signs of life based on carbon structures, and requiring, for instance, liquid water. That is, life that has been supported by and evolved in the very specific terrestrial environment. Generally, recent studies have focussed on the requirements for life to evolve in Earth like environments (Vago & Baglioni 2014; Lorenz et al. 2011).

However, within the definition of habitability, the Earth-like environment may incorporate 'extreme' conditions. Initially, it may be expected that life cannot live in

exceptionally harsh environments: for instance particularly high or low temperatures (e.g. the Arctic or in a volcano), very salty locations (the Dead Sea), or in a high radiation environment. However, it has been shown that some forms of microorganisms, known as extremophiles, can indeed survive these extreme environments. Malherbe et al. (2017) describe Raman spectroscopy analysis performed on a gypsum sample (seen in Figure 1.1) from a hypersaline saltern evaporation pond, on which microbial pigments were discovered showing how life had evolved to survive in such a harsh environment. The carotenoids identified on the sample are invaluable for certain microorganisms to survive in such harsh environments, as they absorb green light, preventing significant damage to the biomolecule, hence allowing it to survive in the hyper saltern environment (Telfer 2005). Similarly, Edwards et al. (2010) performed Raman spectroscopy analysis on a sample from a hot (60°C), saline environment in which they noted key characteristics of biomolecular compounds. Identification of materials, such as evaporitic minerals and carbonates and sulphate materials, indicated the process of cyanobacterial colonisation (Howell G M Edwards et al. 2010). It has been shown that materials, such as carotenoids, are produced to protect the organisms in extreme environments (and hence support reproduction and evolution), and that they are detectable by instruments such as Raman spectrometers. Therefore, using the analytical instruments, it is possible that such signs of life can be identified in harsh environments on other planets or moons. Hence, when searching for life, extreme environments are not to be discounted.



Figure 1.1: Microbial pigments on a gypsum sample from a hypersaline saltern evaporation pond in Israel. (Malherbe et al. 2017).

Initial exploration of the Solar System has been able to identify numerous planets and moons where liquid water has existed in the past or is currently present on or below the surface. However, despite these discoveries, it is not certain that these bodies are habitable and can support life. To confidently confirm (or otherwise) habitability, it is necessary to perform in-situ measurements of the surface and subsurface of the body. Through various analytical techniques (such as Raman spectroscopy and X-ray Fluorescence Spectroscopy), it is possible to determine and analyse the composition (e.g. molecular, elemental, or mineralogical) of regions on the planet/moon. Such analysis can provide a more detailed and clearer understanding of the geological and geochemical processes that may or may not have once occurred, and environmental evolution throughout the body's history.

The first step in the search for life elsewhere in the Solar System began on Earth's nearest neighbour Mars (Klein 1977). With landscapes similar to those seen on Earth, Mars has always been of interest in the search for life. As recently as July 2018, Mars Express, a European mission to Mars, discovered evidence of liquid water trapped under the ice of the Martian south pole (Orosei et al. 2018). If liquid water was present on Mars in its early history, and with an atmosphere potentially similar to Earth's (before it was removed), could life have evolved on this planet, as it did on Earth? Mars' two moons, Phobos and Deimos, whose origins are currently unknown, may also hold information that could provide more detail on early Martian history, or even to how life originated on Earth. Two main theories are that they are accreted from a large impact on Mars in its early history or are captured asteroids from the early Solar System. In both circumstances, performing in-situ measurements of the moons and determining their composition and habitability can provide a significant step forward in the search for life. If they are captured asteroids, they can help to provide information on the composition and geological evolution of the types of materials distributed around the early Solar System - it is possible that bacteria or other early forms of life could have been supported on such bodies (one such body carrying early forms of life may have reached Earth). However, if they are found to be accreted material from the early Martian surface, they may provide information on the geology of the planet and could potentially provide more information on the habitability of the early Martian surface (Citron et al. 2015).

There is strong evidence that liquid water is present on a number of bodies in the Solar System, such as the moons Europa (a moon of Jupiter) and Enceladus (a moon of Saturn). Furthermore, (as detailed in Section 1.1 Europa) there is evidence that both moons are likely to have thermal heating within the ocean (for example, in the form of plumes originating from below the icy shells, as well as apparent tectonic features on the moons' surfaces, implying regular movement below), mixing nutrients from their cores with the ocean. The combination of water, energy, and nutrients may be sufficient to support life (Cockell et al. 2016).

However, the accessibility of some of these bodies as well as an ability to acquire the necessary data to search for the particular biomarkers (an indicator of biological states and/or processes) present a number of complex engineering issues. For instance, Phobos and Deimos exhibit an extremely weak gravitational field and, hence, placing a rover or lander to perform on the surface in-situ measurements may be complex and may result in a more expensive mission. Europa is known to have a high radiation environment (e.g. the plasma flux from Jupiter) (Pappalardo et al. 2013; Garrett et al. 2012), which could potentially damage and degrade scientific instrumentation (without appropriate shielding). Even on Mars, it is expected that the surface (that has been analysed by various landers and rovers) has been affected by solar radiation (as there is a lack of atmosphere (Mahaffy et al. 2015) which would reduce the amount of high energy particles interacting with the surface) and hence may not be fully representative of the nature of the early Martian surface and atmosphere. Therefore, acquiring material from below the surface, away from where radiation has an effect (most of the high energetic particles will have been absorbed by the top few metres of the surface and hence material below will be less affected by the radiation) (Ehresmann et al. 2018; Köhler et al. 2016), is vital in providing a clear understanding of the geology of the planet. As well as potentially degrading/affecting the materials on the surface of the moon, the hazardous environment can also damage the mission instruments (for example, Hardy et al. 1998; Skottfelt et al. 2016; Centurelli et al. 2018). The radiation effects can significantly reduce the instrument's ability to acquire good quality data, or cause it to be unusable (for example, Moscatelli et al. 2016; Wages et al. 2018).

Using data acquired from remote sensing instruments from the planet/moon, it is possible to find analogue samples on Earth that replicate the key components, such as molecular and chemical structures, as well as analogous geological and biological processes. These analogue samples can be used to characterise the instrument, confirming or otherwise, the capability of the instrument to identify such key components, which are necessary for satisfying the mission science requirements. For example, if a science objective is to determine whether liquid water is present below the surface of Mars, the instrument must be designed and operated to acquire and measure the predicted molecular and elemental structure (that is, for example, the signal to noise ratio of the system must be such that the data can be confidently differentiated from noise, and that the dynamic range of the system must be able to discern between different pieces of information).

This chapter explores the scientific reasons why Mars and its moons, Europa, and Enceladus are key bodies in the search for life in our Solar System. In each section, a detailed summary of current knowledge is provided, and evidence is outlined that supports the theory that water may have been, or is currently present, on the body. A summary of the upcoming mission opportunities, along with specific science objectives, is then provided, highlighting the need for particular measurements to be made and instruments to be optimised for these measurements.

1.1 EUROPA

Europa (along with its neighbours Ganymede, Callisto, and Io) were discovered by Galileo on January 7th 1610 (but named by Simon Marius based on Ancient Greek mythology). The discovery of these bodies orbiting another planet was revolutionary at the time: it proved that the Earth was not orbited by everything observed in the sky, nor that our planet was the centre of the universe.

Europa, the smallest of the four Galilean moons orbiting Jupiter, is of major interest for upcoming missions, particularly in the search for life. From the data obtained by the Galileo spacecraft in the 1990s (Pappalardo 2012) and more recent terrestrial observations (Ligier et al. 2016), it has been hypothesised that there is a deep subsurface ocean, which is in contact with the mineral core of the moon, both enclosed by a thick, solid icy shell (Carr et al. 1998; Pappalardo et al. 1999), illustrated in Figure 1.2. It is, therefore, important to determine the habitability of this terrestrial body: the abundance of liquid water interacting with nutrients from the mineral core, as well as energy from the thermal movements within the ocean (theorised from observations of water plumes from the icy shell (Jia et al. 2018)) are all key ingredients for life.



Figure 1.2: The trailing hemisphere of Europa, one of Jupiter's moons (credit: NASA/JPL-Caltech/DLR)

A desired location in the search for life, Europa plays a central role in understanding the habitability of icy worlds throughout our Solar System and beyond. Life on Earth may have originated from hydrothermal systems on the ocean floor: a dark location where photosynthesis occurs despite the lack of light (Dodd et al. 2017). Finding life on Europa, a body located approximately 780 million km away from the sun, may support this theory and could help to underpin the idea that life can form without sunlight on other terrestrial bodies (Pappalardo et al. 1999). Furthermore, studying Europa can enhance the understanding of the processes that have led to the diversity of the Jovian system and the interactions between the system's numerous bodies. Exploring the moon can advance the scientific understanding of how satellites around gas giants can form, as well as fundamental aqueous and geochemical processes in the solar system (Zhu et al. 2017; Zolensky et al. 2017). Therefore, a number of space agencies, such as NASA, are keen to send comprehensive suites of analytical instruments to the moon within the next couple of decades (Hand et al. 2016).

A number of missions have remotely acquired spectra and images of Europa from flybys, satellites, and telescope observations. The missions which observed the moon of Jupiter included Pioneer 10 in 1973, followed by Voyagers 1 and 2, Galileo, New Horizons, and the Deep Space Network. At the same time as these missions reached the moon, models were under development demonstrating that the internal heat of the moon, and specifically tidal heating, can be sufficient to support an ocean under a thick icy shell (Consolmagno & Lewis 1978; Fanale et al. 1977). This internal heating was thought to be generated and maintained by the pressure caused by Jupiter's gravitational field (Cassen et al. 1982; Squyres et al. 1983; Schenk et al. 2004; Zimmer et al. 2000).

The first few images that supported the theory that Europa had an icy shell came from the Voyager mission (evidence was acquired by the Galileo mission in the late 1990s, which supported the hypothesis that an ocean existed (Squyres et al. 1983)), an example image visible in Figure 1.3. With a resolution of 2km/pixel, Voyager's images revealed a bright icy surface scarred with an intricate pattern of ridges and apparent fractures. Perhaps the most surprising feature from these images was the lack of impact craters (Squyres et al. 1983): Jupiter's relatively strong gravity attracts a high number of asteroids and comets which likely regularly interact with the other bodies in the Jovian system. Therefore, it is expected that the icy moon has been heavily bombarded during its lifetime. The proposed sub-shell ocean could cause regular tectonism and resurfacing, as such 'healing' the surface from such impacts. This movement is also supported by the imaged ridges and fractures.



Figure 1.3: An example of the images of Europa taken by Voyager, highlighting the ridges and fractures and lack of craters (Squyres et al. 1983).

The suggestion that an ocean might exist beneath the apparent icy shell remained unconfirmed until the Galileo orbiter performed a number of flybys of the moon between 1996 and 2000 (Anderson et al. 1998; Thomas et al. 2017). The first images returned from the mission's Solid State Imaging experiment exhibited clear features that strongly indicated the presence of near-surface liquid water or ductile ice at the ridges (Pappalardo et al. 1999). Furthermore, Anderson et al. (1998) used data from the radio Doppler instrument onboard the mission to help model the internal structure of the moon as a three-layered body with an iron (or iron-sulphide) core, covered by a rocky mantle, and surrounded by water (of a thickness 80-170km). However, despite the data acquired, it was not possible to verify whether the water layer was in the liquid state. Rather, the most compelling evidence came from the magnetometer data. Jupiter's magnetic field was shown to be tilted at an angle of 10° from its equatorial plane and the four Galilean moons (Pappalardo et al. 2013). Due to the planet's rotation and the moon's orbits, the effects of the field's varying polarity on the timescale of the planet's rotation (~11hours), resulted in an induced magnetic field around the moons. For the magnetic field to have been induced in these bodies, some sort of conducting layer must exist and, currently, the favoured theory for a conductive material in the moons is salt water. It was not until near the

end of the mission's lifetime in 2000 that Europa's induced magnetic field was measured and verified by the satellite, hence providing strong evidence for a subsurface ocean (Pappalardo et al. 1999; Fagents 2003; Phillips et al. 2000).

The data collected by the instruments on the Galileo mission also helped to further develop the theory that the moon's outer shell (the lithosphere) undergoes constant resurfacing, resulting in the surface appearing relatively younger than the calculated age of the moon (Carlson et al. 2009). Earlier models predicted a large number of impact craters on the surface of Europa (Schenk & Turtle 2009) due to the influx of impacts caused by Jupiter's strong gravitational field, but only 23 craters larger than 10km in diameter were observed (Schenk & Turtle 2009). Furthermore, the depths of the largest craters are much shallower than those of similar size on other icy bodies or terrestrial planets. This difference may be caused by the shell being warmer than other measured icy lithospheres during impact (Schenk & Turtle 2009). Moreover, the images of the surface show features such as double ridge morphology – a distinct feature caused by the rise of warm water along any fractures and the tectonic movement of faults. Heat would be generated from rubbing between the faults, melting the ice, and creating a flow of water underneath to form the ridges and elevated shapes imaged on the surface (Nimmo & Gaidos 2002). This geological model is also consistent with the features imaged from Voyager.

Another compelling feature imaged on the surface is the dark brown material, observed on a number of different locations on the surface, contrasting with the bright icy features apparent across the rest of the surface. Spectral analysis of these sites strongly suggests the presence of hydrated sulphate salts and hydrated sulphuric acid (De Angelis et al. 2017; Thomas et al. 2017; Dalton et al. 2005; Carlson et al. 2009). These materials are expected to originate from the moon's core and/or its subsurface ocean. These data, therefore, support the model proposed that material is transported from the core and the ocean to the surface, likely from the internal/tidal heating. Interestingly, these spectrally analysed materials are not typically found to be dull and brown in colour; rather it is expected that the material has been affected by Europa's high radiation environment (Carlson et al. 2009).
More recently, at the end of 2012, a significant discovery was made by the Hubble Space Telescope whilst observing Europa: UV emission lines of oxygen and hydrogen (identified as water vapour plumes) were observed near the South polar region of the moon (Roth et al. 2014; Sparks et al. 2018). The apparent plume activity lasted 7 hours. Analysis of the plumes demonstrated that they reached a maximum height of approximately 200km, and exhibited a kinetic temperature of 230K (Roth et al. 2014). No plumes were observed in the month prior to this discovery, nor in 1999 or when the observations were made again in 2014 (Jia et al. 2018). The lack of plumes during the observations imply that they are temporal, or were caused by a significant event (Jia et al. 2018). Either way, the successful observation of the plumes helps to further prove the presence of water and internal thermal heating and movement in the moon, all of which are necessary ingredients to support life (Jia et al. 2018; Roth et al. 2014).

1.1.1 Mission Opportunities

There is compelling evidence for the presence of both an ocean of water on Europa and a source of internal heating/energy and movement of nutrients from the core to the icy surface (Pappalardo 2010; Pappalardo 2012; Carlson et al. 2009). However, there are still features and characteristics that require detailed characterisation in order to understand and enhance our insight into the moon's habitability and ability to support life. For instance, developing a more detailed geological model of the moon's internal structure, and specifically the ocean, can establish constraints on the possible biological and chemical evolutions of the materials; developing our understanding of the pressure-temperature constraints, water-to-rock ratios, and kinetic processes involved (Pappalardo et al. 2013). Furthermore, determining the spatial distribution of liquid water in the icy lithosphere can provide a clearer view of the possibility of temporary habitable regions that may support life varying from, and in a different location, to the ocean. Moreover, performing in-situ measurements is undoubtedly invaluable for furthering our knowledge about the material present on the moon and in the ocean, providing a much more conclusive view of the likelihood that life exists on Europa.

Since the success of Galileo, space agencies have begun focussing their efforts on Europa, for the search for life. In 2007, a team of scientists put forward the concept mission LAPLACE to ESA's Cosmic Vision Programme. Blanc et al. (2009) provided an argument for the Jovian system being an analogous Solar System, suggesting Europa could be positioned in the system's habitable zone. They presented the need to not only have a dedicated mission to Europa in order to analyse its habitability, but also to the Jovian system as a whole, to further our understanding of whether the system (and its creation) played an influential part in evolving the habitability of the moon. They proposed a trio of multi-platform and multi-target architecture orbiters to achieve the science goals of the mission.

In the following year, the LAPLACE team combined with the NASA Europa Explorer Study team (who had been working on a potential mission to the Jupiter and Saturn systems) to form the Joint Jupiter Science Definition Team, resulting in the proposal of the Europa Jupiter System Mission (EJSM). In 2009, EJSM was chosen by NASA as a flagship mission. The mission would be comprised of two spacecraft: the NASA led Jupiter Europa Orbiter (JEO), and the ESA led Jupiter Ganymede Orbiter (JGO). Both would orbit Jupiter and the four Galilean moons for 2.5 years (Prockter et al. 2011), after which JEO would spend 9 months focussed on analysing Europa's geology, interior structure, ice shell, composition, and local environment (and IGO would perform similar measurements at Ganymede). An example of the internal structure of the four moons the EJSM would aim to confirm (or otherwise) is shown in Figure 1.4. Unfortunately, by the end of 2010, this mission was not funded, as it was argued that it did have strong endorsement from the NASA commission NRC Planetary Decadal Survey (Prockter et al. 2011) and was too expensive. The National Research Council (NRC) stated that, although Europa is an interesting scientific target, a dedicated mission would not be funded unless the price of it was significantly reduced and/or funding was provided from elsewhere.



Figure 1.4: An example of the proposed internal structures of the four Galilean moons. Europa is top right, being the only moon with the ocean (blue) being in direct contact with both the icy surface and core of the moon (Clark et al, 2011).

After the cancellation of EJSM, ESA devised a new mission based on JGO: Jupiter Icy Moons Explorer (JUICE). The mission's aims include determining to what extent the Jovian system is a miniature Solar System (and can be used as a representative for those other than our Solar System); analysing the planet's magnetosphere and atmosphere; and the planet's satellites and rings (Dougherty et al. 2011; Grasset et al. 2013). Specifically, for 3 years of its mission lifetime, it will analyse Jupiter's circulation, meteorology, chemistry, and structure from the cloud tops to the thermosphere. The focus will then move to Ganymede and the habitable zone for the three icy moons (Grasset et al. 2013).

Using the data collected from the JEO studies (Europa Study Team 2012), NASA designed another mission to satisfy the Decadal Survey requirements and to meet the engineering challenges of such a mission: Europa Clipper, also known as the Europa Multiple Flyby Mission (EMFM) (Pappalardo & Goldstein 2013). The aim of the mission was to launch a satellite to orbit Jupiter (hence avoiding the high radiation environment of the moon) and image and perform measurements of Europa during flybys. During each flyby, it would aim to acquire data on the surface and subsurface, as well as identifying materials in the moon's atmosphere, and measuring the gravitational and magnetic field. These measurements aimed to fulfil

the main science objective of exploring the habitability of the moon (Phillips & Pappalardo 2014). This mission is currently in the preliminary design and technology completion phase until the end of 2018.

In 2016, NASA initiated a pre-phase A mission concept study for a Europa lander (Hand et al. 2016). The aim was to follow the EMFM and perform the first in-situ analysis searching for life since the Viking mission on Mars 50 years earlier. The Europa study team defined the science goals of the missions, highlighted in Figure 1.5, in terms of hierarchy and prioritisation. The team developed a science traceability matrix following the main objectives through to the measurements required for each, and drafted a detailed mission concept and payload. The lifetime of the lander was suggested to be 20+ days on Europa's surface, for a baseline surface operations phase in which five samples (each acquired from 10cm below the surface), would be processed and analysed.

The science goals for the Europa lander mission, defined by the Europa study team (Hand et al. 2016), are as follows:

- 1. Search for evidence of life on Europa;
- 2. Assess habitability of Europa via in situ techniques;
 - a. Remove ambiguities with detecting signs of life; determine composition of sample surface material;
- 3. Characterize the surface and subsurface to enable future robotic exploration;
 - a. Frame Europa as a potentially active and dynamic ocean world; ensure future robotic missions can explore landscape or deeper within the ice shell and ocean;
 - b. Provide extensions and enhancements of observations of EMFM.



Figure 1.5: The science goals of the Europa Lander Mission. The image highlights how each objective overlaps. The goals are represented with each letter: goal 1: "L" for "life," goal 2: "h" for "habitability," goal 3: "c" for "context." (Hand et al. 2016)

The science goals proposed by the study team aim to meet the requirements set out by the NRC Decadal Survey: to discover habitable environments and life on alien worlds, and to perform measurements which are otherwise not possible from flybys or orbiters (Sciences 2011). The study team also stated that the mission was linked with the science priorities for outer solar system exploration, as laid out by the Decadal Survey, focussing on the study of organic chemistry and possible biosignatures. Moreover, the Europa lander mission also addresses three of NASA's "14 Big Questions" for planetary exploration as well as NASA's Science Plan, helping to answer the main question of "is there life beyond Earth" (Hand et al. 2016).

The study team strongly suggested focussing efforts on improving miniaturised instruments for robotic spaceflight missions, specifically targeting the search for life.

A highly recommended analytical technique that could satisfy the Europa lander mission goals (of identifying organics and inorganics) is Raman spectroscopy (Hand et al. 2016; Wang, J. Lambert, et al. 2016; Wang, J. L. Lambert, et al. 2016; Edwards, Moody, Jorge Villar, et al. 2005; Howell G. M. Edwards et al. 2010). A dual wavelength Raman spectrometer will be proposed (Wang et al. 2018) for this mission as a key identifier for life detection (described in detail in Chapter 2). The science goals of the instrument will be to identify organic compounds and detect structural compositional, or functional indicators of life (science goal 1); determine the extent of the habitability of the moon's ocean and analyse the spatial variability in the habitable zones (science goal 2); and help to characterise the chemical and mineralogical composition of the surface, and the physical and chemical processes that affect the moon's materials (science goal 3) (Hand et al. 2016). Furthermore, current focus is on miniaturising Raman spectrometers for space missions (Vítek et al. 2012; Malherbe et al. 2017) in order to reduce the mass and volume of the instrument (to satisfy the engineering budgets of the mission). Specifically, in this thesis, the focus will be on the design and optimisation of a miniaturised Raman spectrometer, a compact instrument suitable for a Europa lander. A number of critical instrument design trade-offs are performed to determine the optimum design of the instrument (including adequate instrument performance effects of Europa's high radiation environment on the instrument) for the engineering budget of the mission to satisfy the mission's science goals. The camera system will then be fully characterised to meet the science objectives of the mission.

1.2 MARS

During the first observation of Mars through Huygens and Cassini (which were used to determine the Martian orbital parameters) significant changes to the Martian surface between observations were noticed. Through the observations, it was assumed that the red planet had an atmosphere with similar properties to Earth's, strengthening the interest for confirming the presence on life on another planet. Furthermore, spectral data obtained from light reflected by the Martian surface showed a lack of chlorophyll in the dark patterns, hence disproving the idea that vegetation was present on the surface. Following this, Schiaparelli and Lowell proposed the possible existence of canals on Mars in proximity to irrigated land (Zahnle 2001). However, theories of the presence of vegetation on Mars were questioned due to the planet's environment being too cold to support vegetative life. Furthermore, Mariner 4 returned surfaced images that reinforced the presence of "canals", as seen in Figure 1.6, but also confirmed a dry surface and a lack of vegetation.



Figure 1.6: An image sent back by Mariner 4, one of the first images illustrating Mars' dry, rocky, and cratered surface. (Credit: NASA, 1965)

When the first probes reached the planet, it was possible to characterise Mars' topography and clear fluvial features were identified. The Viking programme was launched in the 1970s (Levin 2015). The scientific objectives of the Viking programme were: to obtain high-resolution images of the Martian surface; characterise the structure and composition of the atmosphere and surface; and (with special emphasis) search for evidence of life on Mars. The mission consisted of launching two identical spacecraft (each with an orbiter and a lander) carrying an IR spectrometer, a gas chromatograph mass spectrometer, and an X-ray fluorescence instrument (Soffen 1977).

Pre-launch instrumentation tests mainly focussed on the ability to detect microorganisms, with the design of the panoramic cameras also aimed at imaging the local environment in an attempt to find larger, more complex organisms (Klein 1977). It was also expected that due to impacts of carbonaceous chondrite meteors there would be a presence of organics detectable by the Viking instrumentation. Measurements showed that >100m of the mantle material had somehow been stripped away and that resurfacing of the planet (from analysis of the number of craters of diameter <100m) seemed to still occur (Thomson & Schultz 2007). Identification and analysis of larger craters helped to support the theory of the Hesperian age (a period of time on Mars in which there was substantial volcanic activity), which also provided a rough estimate on the age of the planet's mantle (Thomson & Schultz 2007). Although a small number of organics (not the number that were expected) were measured by the instruments, it was inconclusive as to whether they had been deposited by meteorites or actually indicated previous/current processes of chemical evolution on the planet (Klein 1977; Navarro-González et al. 2006; Navarro-González et al. 2010). It was suggested that the lack of organics measured may have been caused by photodestruction (Chun et al. 1978), (such as UV radiation), but it was not possible to extrapolate the theory for the entire Martian surface (Chun et al. 1978). Suggestions were made to acquire complementary data from Mars to help confirm, or otherwise, this theory across the planet. Nonetheless, given the data acquired from all Viking instruments, and the geological context of the landing sites, it was not possible to conclusively state whether the small number of organics measured revealed signs of life on Mars. Instead, it was suggested that the organics were due to non-biological processes. More data would need to be acquired to support either conclusion.

It was not until 1996 when the next mission reached Mars: NASA's Pathfinder. This mission consisted of the first rover (Sojourner) to traverse the surface, with the purpose of the mission focussing on demonstrating "faster, better, and cheaper" space exploration technology by launching a suite of instruments significantly cheaper than the cost of the Viking programme. The science objectives were to: analyse the geochemistry, evolution, and magnetic properties of the surface, as well as the magnetic properties of the Martian dust and atmosphere (Rieder et al. 1997a). Building on the engineering configuration of Pathfinder, in 2003 NASA built and

launched the two rovers (Spirit and Opportunity) as part of the Mars Exploration Rover (MER) programme. The science objective of these rovers was to determine the extent to which the planet's environment and geology could support the formation and preservation of prebiotic compounds, and whether life started and evolved on Mars by: analysing the surface's aqueous potential; characterising the diversity of rocks and soils that may reveal information on past water activity; and to assessing whether the possible aqueous environment would support life (Crisp et al. 2003).

In the same year, ESA launched its first mission to Mars with Mars Express, consisting of the orbiter and lander (Beagle 2). The science objectives of this lander included geomorphological characterisation of the landing site; analysis of the oxidation state of the surface; characterisation of the atmosphere; and identification of evidence that may prove, or otherwise, whether life processes may have been supported in the past on Mars (Wright et al. 2003). Even though Beagle 2 successfully landed in 2003, this was not confirmed until 2015, as it only partially successfully deployed its antenna causing scientists to lose contact with the spacecraft (Ward 2015).

In 2008, the next mission (the Phoenix lander), as part of NASA's MER programme successfully landed on Mars near its northern polar region (Parker et al. 2016). The rover's main science objective was to verify the presence of subsurface ice, determine the history of water at the landing site, and analyse the habitability of the polar ice-soil and climate (Kounaves et al. 2010). Following this, NASA's Mars Science Laboratory landed on Mars in 2012, with the aim of assessing the habitability of the landing site, analysing the geology of the environment, characterising the surface radiation, and investigating Martian processes that may influence habitability (Grotzinger et al. 2012).

Although these rovers and landers have not specifically searched for signs of life since the Viking programme, there has been significant scientific return from these missions, providing a much more detailed understanding of the history of the planet. The missions have enhanced the understanding of the habitability of Mars (Vago et al. 2017), potential to support life and its habitability, and have provided a more in depth understanding of the materials, geology, and atmosphere of the planet. Initial

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data indicated that the lack of a significant ozone layer and a lower atmospheric pressure on Mars results in a higher surface flux of UV radiation on the surface and it was known that such a high radiation environment would be a significant challenge for the evolution of life (Cockell et al. 2000). It is likely that the UV radiation penetrates to up to 2m of the Martian surface, and hence life is likely to find shelter below the surface (Cockell et al. 2000). Hence, it is informative to analyse and characterise the materials, and search for signs of life, beneath the surface. No missions has drilled into the surface to collect material unaffected by the radiation (the Curiosity rover utilises a scoop to collect material (Berger et al. 2014)); the first to do this will be the ExoMars rover, detailed in Section 1.2.1 Mission: ExoMars).

Nonetheless, from the previous missions, theories have been proposed that the climate on Mars was different compared to that known today and may have supported water on the surface, in the Noachian/early Hesperian era. The first theory, known as the "cold and dry" theory suggests that water was formed by local thermal energy sources in the cold and dry environment. A second theory, known as the "warm and wet" theory suggests the Martian atmosphere comprised of greenhouse gases, supporting a hydrological cycle, like that currently on Earth (Fairén 2010). However, Fairén (2010) has proposed a third theory, the "cold and wet" theory, stating that previous mission data strongly suggest that the atmosphere's temperatures at the surface never increase above 273K yet there are signs of liquid water (mainly from geological features) implying liquid water moved across the surface. However, the temperature of the surface would need to be kept above 273K for liquid water to be present. One suggestion is that a dense atmosphere consisting of carbon dioxide would result in pressures on the surface increasing the temperature to above freezing point (Pollack et al. 1987); another is that the thermal energy generated from the regular number of impacts would have increased the surface temperature sufficiently to sustain liquid water on the surface (Catling 2014).

As Mars could have potentially supported liquid water, it is therefore a key target for searching for signs of extinct (or extant) life, particularly below the surface (away from the harsh radiation). With the data acquired from numerous locations on the surface (Parker et al. 2016), the next step in Mars exploration is to characterise subsurface materials. Characterising subsurface Martian material is a key focus of ESA's ExoMars mission, which is detailed in the following section.

1.2.1 Mission: ExoMars

In 1996, an exobiology science team defined guidelines for upcoming missions in the search for life. During the meeting, held by ESA, three fundamental requirements were agreed: (i) landing site to be of significant exobiology interest; (ii) samples to be collected from below the surface to avoid alteration by radiation damage and/or surface oxidation; and (iii) each and every sample to be analysed in-situ by a comprehensive suite of analytical instruments (Vago et al. 2017). Based on these requirements, a number of feasibility studies and mission designs were performed, leading to the design of the ExoMars mission, which was approved in 2005 as a flagship mission in the search for life (Vago et al. 2006; Baglioni et al. 2006).

The first part of the ExoMars mission consisted of a Trace Gas Orbiter (TGO) and the Schiaparelli lander (Svedhem & Vago 2016). The objectives of the TGO were to perform measurements on the atmospheric gases and to analyse the surface for possible signs of current life processes. The Schiaparelli lander's main purpose was to test the entry, descent, and landing process and perform surface measurements (Svedhem & Vago 2016). This part of the mission successfully launched at the start of 2016. However, communications were lost with the lander during descent when it reached the planet at the end of 2016 (Blancquaert 2016). Signals were being transmitted up to 50s before the expected landing (Clery 2017); using data from the TGO, analysis suggests that the final descent process occurred too soon resulting in the parachute not working and the thrusters and heat shield (used to significantly slow the landing module) were damaged from use too high up in the atmosphere (Ferri et al. 2017).

The second part of the ExoMars mission will launch a rover to the surface of Mars in 2020, comprising of a drill (which will collect material from up to 2m below the Martian surface) and the Analytical Laboratory Drawer (ALD), consisting of a number of analytical instruments (that will analyse the material collected and delivered by the drill), as shown in Figure 1.7. The rover will traverse a few km across the surface of the planet in the search for traces of past and present life, and will be the first to be equipped with a drill to look at materials under the surface (that is, materials not affected by radiation, weathering, or arising from impacts). It will also be the first mission to incorporate a Raman spectrometer (for molecular analysis of the samples acquired by the drill). The payload on the rover includes (Vago et al. 2017):

- ALD: instruments that will perform analysis on the crushed sample from the drill;
 - MicrOmega, visible+IR imaging spectrometer: to characterise structure and composition of sample, will aid RLS and MOMA in targeting locations on sample;
 - RLS, Raman laser spectrometer: to identify mineral phases at grain scale, determine composition, and establish presence of carbon (organic/inorganic);
 - MOMA, Mars organic molecule analyser: to perform broad-range, very-high sensitivity search for organics;
- Drill: for obtaining samples up to 2m below the surface. Includes temperature sensors and an IR spectrometer;
- Contact instruments: instruments to investigate macroscopic features on outcrops/rocks/soils to provide information on environment;
 - CLUPI, close-up imager: sub-millimetre resolution imager for closeup rocks (50cm), will image samples from drill, may identify morphological biosignatures;
 - Ma_MISS, IR spectrometer in drill: perform mineralogical measurements on drill core;
- Panoramic instruments: provide information on geological context, both at surface and subsurface;
 - PanCam, panoramic camera system: three cameras (two wide-angled, one high-resolution) to image the environment, landing site geology, and target material;

- ISEM, IR spectrometer: to characterise bulk minerology, perform remote identification of water-related minerals, complement data from PanCam in identifying targets;
- WISDOM, ground penetrating radar: to establish subsurface stratigraphy, complements drilling strategy;
- ADRON, neutron detector: to analyse subsurface hydration and possible presence of ice (up to 1m below surface);
- Sample preparation and distribution system (SPDS): to acquire sample from drill, produces particulate material, distributes to instruments in ALD.



Figure 1.7: An image of the ExoMars rover showing the locations of the instruments and drill. (Vago et al., 2017)

The science objectives for this mission are defined as (Vago & Baglioni 2014):

- 1. To search for signs of past and present life on Mars;
- 2. To characterise the water/geochemical environment as a function of depth in the shallow subsurface;
- To study the surface environment and identify hazards to future human missions;
- 4. To investigate the planet's deep interior to better understand Mars' evolution and habitability.

With the main science objective being the search for life, it should be noted the ExoMars team will deem the objective as a success: i.e. what, in terms of this mission, will qualify as a life signature or a process of life biology? In the process of defining whether the sample contains life, there are three specific categories for analysis: morphological structure/processes, chemical structure/processes, and the geological context of the sample.

Microorganisms have been found to form biofilms that can alter the sedimentary structure around them (Davies et al. 2016), creating unique and often repetitive patterns with, for example, carbon-rich ashfall particles (Westall et al. 2011). It is expected that if microorganisms were present on Mars they may be too small to resolve but the affects from the resultant biofilms could be distinguished in the Martian rocks as mineral structures or carbonaceous traps (Westall et al. 2015; Ruff & Farmer 2016); the RLS instrument and ISEM have been designed and characterised to identify such materials. Moreover, it has been found that carbonaceous macromolecules that make up the vast majority of biological matter on Earth can be found in layered sedimentary rocks – it is possible life's remains may have been stored in a similar matter on Mars (Summons et al. 2011). Therefore, is it necessary to target biomolecules associated with microorganisms (for instance, amino acids, proteins, nuclei acids, carbohydrates, etc.), as well as lipids and other structural biopolymers (Georgiou & Deamer 2014), and kerogens (Tissot & Welte 1984). Finally, it is necessary to determine the likelihood that the sample's habitat can maintain an aqueous environment and support such processes that maintain the development of microorganisms, hence providing more confidence that the sample may be a biosignature (Vago et al. 2017).

The ExoMars team have defined a potential confidence scoring system to be utilised when determining the likelihood that life may have been (or is currently) present on Mars (Vago et al. 2017). This scoring system is shown in Figure 1.8. It is with this in mind that the analytical instruments onboard have been designed and optimised to identify such characteristics in the search for life. For example, the RLS instrument has been optimised (described in detail in Chapter 2) to search for organics and signs of biological activity through, for example, trade-offs performed on various components of the instrument to guarantee performance characteristics suitable for acquiring the expected data. An example is the trade-off performed for the detector, ensuring the characteristics (such as dynamic range, spectral response, see Chapter 3) are optimised such that specific Raman bands can be differentiated and that the Raman signal can be confidently identified above the noise of the system. After the trade-offs had been performed, a number of laboratory and field campaigns using prototype versions of the instrument were used to characterise the instrument using Martian analogue sites and samples (Rull et al. 2017; Lopez-Reyes et al. 2013; Balme et al., in review), guaranteeing the instrument would be able to satisfy the science requirements of identifying the various signs of biological processes. This procedure that the RLS instrument team (and the other instruments onboard the ExoMars rover) used for designing, characterising, and optimising the systems to specifically look for signs of life on and beneath the surface of Mars has been utilised in this thesis. That is, through the use of analogue sites and samples, specific instrument designs and models can be optimised for the specific goal of searching for signs of life and analysing the habitability of the moon or planet.



Figure 1.8: ExoMars Biosignature Score, a suggested scoring system for classifying the material ExoMars analyses as life (Vago et al. 2017)

1.3 PHOBOS AND DEIMOS

The American scientist Asaph Hall used the largest refractor telescope in the world at that time, the Alvan Clark 26-inch "Great Refractor", to discover two satellites orbiting Mars: Phobos and Deimos (Hall 1878), visible in Figure 1.9. The orbital period of the inner moon, Phobos, being the smallest period of any moon known to date, has now been calculated to be 7.65 hours.

Hall's discovery was significant because by using the orbital characteristics of the moons, scientists at the time were able to determine an accurate mass for Mars. In fact, they were the smallest moons to be discovered at the time, inspiring scientists to consider and search for smaller moons around other planets. Phobos was the first moon to be observed to have an orbital period less than its parent planet's day (Pascu et al. 2014).

Ever since their discovery in 1877, a relatively small amount of data have been acquired from Mars' moons resulting in little information provided on the composition and origin of the moons, with the most intriguing subject being their origin. The predominant theories are that they are accreted material from a large impact on Mars, that they are remnants of Mars' formation, or that they are captured outer Solar System primitive asteroids (Oberst et al. 2014). Other questions arise with the moons' orbital features: Phobos is moving closer to Mars yet Deimos is moving away. Furthermore, Phobos' surface appears to have scars stretching from the large Stickney crater right across to the other side of the moon, see Figure 1.9(a). Deimos has a completely smooth surface apart from a few craters (which are expected due to space weathering (Murchie et al. 2015)), see Figure 1.9(b).



Figure 1.9: Phobos (a) and Deimos (b) as seen by the Mars Reconnaissance Orbiter (MRO) instrument the High Resolution Imaging Science Experiment (NASA/JPL-Caltech/University of Arizona, 2008 (image a), 2009 (image b))

Although there has not yet been a dedicated mission to explore the moons of Mars, space agencies are currently considering missions to both Phobos and Deimos. Importantly in the search for life, these bodies may help to provide more evidence that life on Earth could have originated from small impactors (G. Cooper et al. 2001). The idea that small asteroids and other forms of material moving around the early Solar System may have carried volatile elements, organics, and even amino acids has been supported by the discovery of amino acids in carbonaceous chondrites (G. Cooper et al. 2001). Therefore, determining the origin of the moons is beneficial as it can provide more information on the evolution of life and dynamics of the Solar System. If they are demonstrated to be captured asteroids, scientists will gain a

better understanding of the composition of the small bodies in the early Solar System. If materials, such as amino acids, are found on them, they provide more evidence that important building blocks of life can survive on these small bodies.

Determining that the moons were accreted from a large impact on Mars will further develop the understanding of the planet's composition in its early history. As detailed in Section 1.2, it is likely that liquid water was present on this planet and that the geology of the planet may have supported life processes. If either of the moons are comprised of the same material, it may provide a clearer and deeper understanding of what Mars was like in its early history, and whether it could support life processes.

If either the theory that they were created from material accreted after a large impact on Mars, or the theory that they were formed alongside Mars are confirmed, information on the characteristics of the moons can enhance the understanding of the formation of the Martian system as a whole.

Another benefit to exploring Phobos and Deimos is that they may be utilised to enable humans to land on Mars. As Pratt & Hopkins (2011) discuss, due to the lower gravity and less dense atmosphere on the moons compared to their parent planet, the required mission ΔV to land on them is much smaller, and this results in lower cost missions.

Some data from the moons have already been acquired by spacecraft as they flyby during missions to Mars. Most of the data has been used to further the understanding of the moons' physical characteristics (Duxbury et al. 2014; Pieters et al. 2014). However, since the 1970s, instruments onboard a number of missions have been sending back global spectra of the moons, particularly of Phobos. These spectra have helped to develop theories for the origin of the moons, explained below.

So far the spacecraft which have acquired data from the moons are (Duxbury et al. 2014):

- Mars flybys: NASA Mariners 4, 5, and 6;
- Mars orbiters: NASA Mariner 9, Vikings Orbiters 1 and 2, Soviet Phobos 88, NASA Mars Global Surveyor, NASA Mars Odyssey (still operating), ESA Mars

Express (still operating), NASA Mars Reconnaissance Orbiter (still operating);

• Mars landers/rover: Viking Landers 1 and 2, Mars Pathfinder, Mars Exploration Rover Spirit and Opportunity (still operating), Mars Surface Laboratory Curiosity (still operating).

The first mission to acquire close-up images of Phobos was Mariner 9 in 1971. Mariner 9's orbit situated outside of Deimos' orbit made it beneficial to capture many images of both moons. The mission successful acquired 214 images in both grayscale and colour (using the red, green, and blue filters). Not only were these the first close-up images but they also allowed a more detailed analysis of the moons' topography than had ever been performed before (Duxbury et al. 2014). Interestingly, these images highlighted the moons' irregularity: they appeared to have an ellipsoid shape, unlike any other moon. Furthermore, using the data sent back from Mariner 9, it was concluded that the moons had an almost synchronous rotational period even though Deimos was moving away from Mars and Phobos was moving towards Mars (Duxbury et al. 2014).

The Viking programme was the second mission to acquire data from the moons, although these spacecraft viewed Phobos and Deimos from the surface of Mars, visible in Figure 1.10. This was the first time that Phobos' perplexing scars were imaged globally and the data also enabled the densities of the moons to be accurately calculated.



Figure 1.10: Views of Deimos (a) and Phobos (b) from the Viking Orbiter 2. The largest crater on Deimos seen in image (a) is ~1.3km across; irregular depressions can be seen in the top left of the image. A large crater on Phobos can be seen in the top right of image (b), which spans 5km across; the scars across the surface of the moon can also be seen in this image. (Veverka & Duxbury 1977)

Pang et al. (1978) used spectral data compiled from Mariner 9 and the Viking landers, as well as ground based photometric data, to theorise that the moons' compositions were analogous to outer Solar System asteroids. They found a comparison between the low and neutral albedos of the moons and the asteroids Ceres and Pallas, hence inferring that their surfaces consisted of carbonaceous chondrites, materials expected in primitive bodies (J.A. 1973; Cronin et al. 1988; Nakamura 1974; Veverka & J. 1977; Zellner & Capen 1974). Pollack et al. (1978) concluded a similar theory by calculating the moon's reflectivity curve from Viking data and found that it is analogous to asteroids composed of carbonaceous chondrites. However, the probability of Mars capturing such a small asteroid was difficult to justify: they explained that only very intricate capture models can demonstrate how this type of body can be captured, whereas more straightforward models imply that it is extremely unlikely that this could have happened (Pollack et al. 1978).

From the 37 images sent back by the Russian probe Phobos 2, Avanesov et al. (1991) determined the density of Phobos to be 1.9 ± 0.1 g/cm³. This value was thought to be surprisingly low and could only be explained by the theory that the body must have consisted of water ice (Murchie et al. 1991) and other similar carbonaceous chondrite minerology (Pajola et al. 2014; Dalle Ore et al. 2014; Britt et al. 2002), for instance with similar composition to that of the Mathilde, Eugenia, and Hermione asteroids (Rosenblatt 2011) (C- and D-type asteroid compositions). Therefore, it appeared that the data collected reinforced the theory that the moons were captured primitive asteroids. However, the theory that small bodies could not have such a low density without any icy composition was later disproved when the Near Earth Asteroid Rendezvous (NEAR) spacecraft sent back data of the asteroid 253 Mathilde, which revealed, using Near Infra-Red (NIR) spectral analysis, that it too had a very low density but that there was no evidence of a hydrated composition (Rivkin et al. 2002). Moreover, the Infrared Mapping Spectrometer (ISM) on Phobos 2 acquired the first infrared spectra of the surface of Phobos, which led to the conclusion that there is a significant lack of hydration on the surface (Bibring et al. 1989).

As stated in Pollack et al. (1978), only models with very specific parameters, and a vast number of physical parameters and variables can satisfactorily explain how Mars could capture asteroids the size of Phobos and Deimos. Hunten (1979) and Sasaki (1990) suggested a scenario where the most likely capture mechanism was the planetary atmosphere's aerodynamic drag. During Mars' early history, its primary atmosphere regularly attracted material from the young Solar System and hence was likely to also capture bodies travelling past the planet. Although both models eventually proved that Mars could capture these small bodies (Hunten 1979; Sasaki 1990), neither could predict how both moons' orbits were nearcircular and near-equatorial. Furthermore, the capture mechanism models did not justify how both moons had synchronous rotational periods (Hunten 1979; Sasaki 1990). Hence, the theory that the moons were asteroids captured by Mars was questioned. Alternatively, the suggestion that these two bodies were co-accreted during Mars' formation or formed from ejecta after a large impact on Mars were favourable. The spectra is therefore expected to reveal a composition analogous to bulk Mars or Martian crust respectively.

The fact that the detailed analyses of the data collected from the various flybys neither confirm nor reject any of the origin theories highlights the importance of a dedicated mission to the moons. Establishing the moons' composition (and hence inferring their origin) can provide more information on where life originated and what types of bodies may support it in the Solar System. If the moons were found to be captured asteroids, they may reveal more information about the compositions of carbonaceous asteroids from the early Solar System, and whether they may have supported and transported life. If it is concluded that they are accreted material from the Martian surface, characterisation of the moons' composition may complement analysis from missions to Mars (for example ExoMars) which aim to characterise the Martian surface, determining whether life may have been present in the planet's early history. Performing in-situ analysis (molecular and elemental) of the moons' surface and subsurface can help to reveal the origins of the moons. Attempts have been made (and are currently being designed) to launch such a mission, as explained in the following section.

1.3.1 Mission Opportunities

So far, there have been no successful dedicated missions to Phobos and/or Deimos. The Russian Federal Space Agency (Roscosmos) first attempted a Phobos programme in 1988. It was planned to be the first unmanned mission to both Mars and its moons. The first probe, Phobos 1, which was launched on 7th July 1988, suffered a power supply failure in September that year, after its attitude thrusters were deactivated. The second probe, Phobos 2, launched four days after the first, managed to return 37 images of Phobos. However, as it was about to deploy the rovers onto the moon, the agency lost signal with the spacecraft and it was ultimately declared a failed mission in March 1989. After this, the Russian Federal Space Agency launched a second mission with their Phobos lander sample return mission, Fobos-Grunt, which was launched in November 2011, and incorporated a satellite from the Chinese Space Agency. Unfortunately, due to the failure of the spacecraft's rocket burns in low Earth orbit, it was deactivated and eventually reentered Earth's atmosphere in January 2012.

Nonetheless, a significant number of space agencies are interested in funding a mission to the moons and there are currently fourteen missions in pre-phase A: eight missions proposed to NASA, three to ESA, one to CSA, one to JAXA, and Russia is re-attempting a simpler version of the Fobos Grunt mission (Fobos-Grunt 2).

A current mission in the design phase is JAXA's Martian Moons Exploration (MMX). The two main science goals are: to reveal the origin of Mars' moons and gain a better understanding of planetary formation and material transport in the Solar System; and to observe processes that impact the Martian system and Martian surface environment (Lawrence et al. 2018). The aim of the mission is to collect >10g of material from the Phobos surface to return to Earth for detailed characterisation.

Each mission concept is currently being conceptualised and proposed to the various space agencies for approval. Given that most of these missions are in pre-phase A, opportunities still exist for recommending new instrument configurations that will maximise scientific return. That is, with detailed analyses of the various scientific objectives of each mission and the capabilities of each instrument configuration, it will be possible to suggest enhancements that will enable substantial improvements in performance and improve the likelihood of achieving each set of science goals. Therefore, in this thesis, the design and optimisation of an instrument suitable for a mission to the moons based on the missions' science goals is described. Analogue samples of the moons are characterised using Raman spectroscopy, UV spectroscopy, and XRF spectroscopy, with the aim of providing a suggestion for the optimal instrument design and configuration for a mission to the moon, to analyse the surface of the moons and hence determine their origin.

1.4 ENCELADUS

The eighth moon of Saturn, Enceladus, was discovered by William Herschel in 1793 whilst using the (then) largest telescope for the first time (Herschel 1795); it was, and still is, challenging to observe. As it orbits so close to Saturn (3.94 Saturn radii), the scatter of light from the planet and rings (Spencer et al. 2006) causes difficulties in resolving the moon. However, at the time Herschel observed the moon, the Earth

was positioned in the plane of the rings, (at the Saturn equinox) reducing the glare from the planet and its rings, allowing the moon to be clearly observed.

Initial terrestrial observations revealed that the moon's surface is composed of almost pure ice (Cruikshank 1980), arguably with ammonia ice (Emery et al. 2005). Smith et al. (1982) and Verbiscer et al. (2005) calculated the visual geometric albedo to be relatively high (consistent with snow or ice) compared to any other known Solar System body. Before the Cassini mission in 2005, only Voyager 2 had managed to image the icy moon. Analysis of data sent back from the mission indicated that parts of the surface exhibited a noticeable lack of craters (Smith et al. 1982), in a similar observation to those made on Europa's surface. The lack of craters suggests that the surface constantly undergoes resurfacing, potentially via endogenic forces resulting in the observed youthful parts of the surface (<200 million years old) (Smith et al. 1982; Kargel & Pozio 1996). In fact, even the heavily cratered parts of the surface show signs of resurfacing inside the craters.

As with Europa, the vast majority of the data collected from the icy moon Enceladus came from one satellite performing measurements during a number of flybys. Since 2005, the Cassini Saturn Orbiter has made significant discoveries whilst sampling the plumes ejecting from Enceladus' south pole. From initial measurements acquired in the first half of 2005 (Spencer et al. 2006), the surface of Enceladus was shown to be largely covered by water ice and to exhibit many scars due to tectonic activity, with a number of networks of ridges and troughs alongside relatively old cratered parts (Spencer et al. 2006), as well as a large number of plumes ejecting from the south pole. The onboard gas mass spectrometer characterised the plumes, see Figure 1.11, whilst moving through them and demonstrated that they were composed of water vapour, nitrogen, and carbon (including organics) (Waite Ir et al. 2009). The Cosmic Dust Analyser instrument determined that the ice grains found in the plumes contain sodium and potassium salts (Postberg et al. 2011). The discovery of the salt in the plumes water vapour led to a theory that the plumes were ejected material from seawater on the moon (Jia et al. 2018). Moreover, the silica grains discovered in the plumes strongly indicated the circulation of water inside the warm rock on the moon's ocean floor (Hsu et al. 2015). Observations of the mass spectra of the emitted ice grains found that they contained complex

macromolecular organic material with molecular masses above 200 atomic mass units (Postberg et al. 2018). Furthermore, the abundances of the material measured by the two instruments suggest the plumes originate from an alkaline hydrothermal system, analogous to those in a number of places on Earth's ocean floor (Glein et al. 2015).



Figure 1.11: A representation of a cutaway of Enceladus illustrating the theorised hydrothermal activity in the moon's ocean causing the plumes seen by the Cassini spacecraft. (Credit: NASA/JPL-Caltech, 2015)

The plumes from Enceladus' polar region could originate from active melting or from a source of liquid (for example, an ocean). However, the observed salt grains strongly support a liquid reservoir theory (Thomas et al. 2016), which is maintained in a liquid state by the moon's elliptical orbit, resulting in tidal dissipative heating (Travis & Schubert 2015; Choblet et al. 2017). Therefore, a well-supported theory is that the material/nutrients (such as salt and silicates) are transported from the porous core and ocean floor via hydrothermal activity inside the porous core, resulting in the plumes that have been observed by Cassini (Hsu et al. 2015b; Sekine et al. 2015; Waite et al. 2017). As plumes have been observed on multiple acquisitions, hence strongly inferring thermal movement (and with the nutrients measured in the plumes), Enceladus is a key destination for a mission in the search for life. It has been stated that for life to be supported on a body, liquid water, nutrients, and a source of energy must be present. Therefore, a number of key measurements that would be vital in a mission to the moon would include confirming (or otherwise) that the salt observed in the plumes originates from the ocean floor. It is also necessary to confirm (or otherwise) that the subsurface ocean

consists of liquid water as opposed to another material, which may not support life. Therefore, with the data acquired from Cassini, Enceladus appears to be a candidate for a habitable environment, and may support life. In-situ molecular and elemental analysis (for example, through Raman spectroscopy) should be utilised for establishing the compositions and geological evolution of the moons in detail, whilst searching for signs of past or present life. Furthermore, if life were to be discovered on Enceladus, it may complement data from missions to Europa: as the moons appear to have a similar structural compositions (subsurface water ocean below an icy shell, with both moons revealing signs of tectonic movement on the surface) and internal heating, if signs of biological process were to be discovered on one, it may provide contextual support for measurements made on the other moon. These measurements could then be extrapolated for other moons both inside and outside of the Solar System that appear to have similar compositions and structures.

1.5 THESIS BREAKDOWN

This chapter sets the scientific context for planetary exploration missions that focus on the search for life. In particular, the current and future missions planned by a number of space agencies are described.

Chapter two discusses the various analytical techniques that could be used by landers or rovers to interrogate surface material on each planet or moon described in Chapter one.

Chapter three then describes the fundamental components in such analytical instruments, and, in particular, focusses on the performance of camera systems in hostile environments. The current technology available for the development of cameras (that will help to make significant steps forwards in terms of understanding the physical processes associated with the material found on the surface of the planet/moon) is described.

Chapter four outlines the development of a complex camera system software model that enables performance to be predicted as a function of radiation environment, thermal environment, excitation source, operating modes, etc. The model is specifically used to investigate the performance of a Raman spectroscopy/context imager instrument in the harsh environment at Europa (the material to be analysed by the instruments in outlined in this chapter).

Chapter five describes the test performed on a representative detector when subject to the harsh environment expected on Europa. The detector was irradiated with a range of fluences to monitor the degradation of the detector performance when operating in such hostile environments.

Chapter six outlines the design and characterisation of a camera system that utilises a number of analytical techniques on the same detector, providing greater scientific return for low mass, volume, and power. Europa analogue samples were analysed to demonstrate the performance of the detector, particularly suitable for a mission to Europa.

Chapter 2 Analytical Science

Chapter 1 described why Europa (and other bodies in the Solar System) are a key locations for analysing habitability and searching for signs of life. When performing such analyses, it is advantageous to acquire a wide variety of information on target composition (such as elemental, molecular, and mineralogical information) to provide a more in depth and clearer understanding of the geology of the Solar System body. However, engineering and cost budgets require trade-offs to be performed in order to prioritise the analytical techniques that should be included on the mission. Here, a variety of analytical techniques are discussed and assessed to determine which combinations are optimal in terms of identifying signs of life on a planet or moon, such as Europa, Mars, and Phobos and Deimos.

There are a number of different analytical techniques that can be exploited to achieve the science goals of a mission. In this chapter, 3 different analytical techniques are described and compared: Raman spectroscopy, UV and visible spectroscopy, and X-ray fluorescence spectroscopy. A description of how each technique can be utilised in the search the life is provided, as well as the typical instrumentation configuration adopted. An assessment of the suitability of the technique for a mission to Europa and the other bodies is also provided.

2.1 RAMAN SPECTROSCOPY

2.1.1 The Raman Spectroscopy Technique

Raman spectroscopy is an analytical technique based on the inelastic scattering of incoming light by molecules in a sample. The effect was theorised by Smekal in 1923 (Smekal & Adolf 1923) and observed by Raman & Krishnan in 1928. Sir Chandrasekhara Raman discovered the technique using liquids (whilst Landsberg and Mandelstam observed it in crystals) and was awarded the Nobel Prize in 1930 for the discovery (Singh 2002). Since then, the technique has been utilised in a vast

range of applications including: medical and pharmaceutical imaging identification and validation of pieces of artwork; characterisation of ivory (Edwards et al. 1998); and in security for detection of explosive materials (Eliasson et al. 2007).

When a photon of a particular frequency interacts with a sample, two types of scattering will occur: Rayleigh and Raman scattering. In Rayleigh scattering, the incoming photon will elastically collide with the nucleus of the target molecule and the cloud of electrons orbiting the nuclei is polarised. When only the electron cloud is distorted there is a very small change in frequency between the incoming and scattered photon as the electrons are relatively low mass. Blue light is scattered more efficiently than red light, as it varies with frequency, *v*, by the relation v^4 (in Rayleigh scattering, the intensity from the dipole scatterer varies $I \propto \lambda^{-4}$ (see equation 2.7)). This process is the dominant scattering process in nature. Raman scattering arises when inelastic scattering occurs: in this case the interaction causes nuclear motion in the molecule, transferring the energy from the photon to the molecule (or vice versa). As the nucleus is significantly heavier than the electron, Raman scattering occurs much less often, in every $10^6 - 10^8$ photon interactions.

At room temperature, in both scattering processes, almost all molecules vibrate in the ground state (lowest energy level). The polarisation of the electron clouds excite the nucleus to a short-lived 'virtual' state, determined by the frequency of the incoming photon. When this inelastic scattering process causes the molecule in the ground state to scatter and transition to a higher energy vibrational state, a process known as Stokes scattering. However, when the initial molecule is present in a higher energy state (due to thermal fluctuations) the interaction can cause the transfer of energy to the photon, causing the molecule to transition to a lower state. This process is called anti-Stokes scattering. A schematic of the three scattering processes described in this way is illustrated in Figure 2.1. The probability as to whether Stokes or anti-Stokes scattering occurs is dependent on the population of molecules in a particular state, described by Boltzmann's distribution (that is, the population of the molecules in a particular state increases with temperature). At room temperature, the population of molecules in a state higher than the ground state is relatively small (than the population of molecules in the ground state) and hence Stokes scattering is much more likely to occur.



Figure 2.1: The three main forms of scattering: Rayleigh scattering, Stokes Raman scattering, and anti-Stokes Raman scattering.

The number of possible vibration types for a molecule is described by the degrees of freedom (the description of the molecule's translation in space): 3N - 6 for all molecules except for linear molecules, which exhibit 3N - 5, where N is the number of atoms in the molecule. Therefore, a diatomic molecule will have 1 mode of vibration, described as symmetric about the centre of the bond. A triatomic molecule will have 3 modes of vibration: a symmetric stretch, a bending/deformation, and an asymmetrical stretch. A schematic illustrating the three possible modes of vibration for H₂O is shown in Figure 2.2. In this diagram the arrows and lines represent the bond(s) between the atoms, which are represented by the spheres. Stronger bonds and lighter atoms will exhibit higher frequencies of vibration, whereas weaker bonds and heavier atoms will result in lower frequencies. The displacement of the vibration of the system can be described according to the equation

$$Q = Q_o \cos(2\pi\nu t) \qquad (\text{eq. 2.1}),$$

where Q is the total displacement of the atoms at time t, Q_0 is the equilibrium position of the atoms, v and is the molecular vibration frequency.



Figure 2.2: Examples of the possible vibration modes of a triatomic molecule (H₂O in this diagram).

As the incoming photon has its own oscillating electric field, when it interacts with the molecule, the electron cloud (encompassing the target's nuclei) is altered, resulting in a change of dipole moment or polarisation. The strength of the induced polarisation is defined as

$$P = \alpha E \qquad (eq. 2.2),$$

where *E* is the incident electric field and α is the polarisability of the molecule, which will be modulated by the molecular vibrations such that

$$\alpha = \alpha_0 + \left(\frac{\delta \alpha}{\delta Q}\right)Q + \cdots$$
 (eq. 2.3),

where α_0 is the polarisability of the molecule in equilibrium. If the electric field, *E*, of the incoming photon oscillating over time, *t*, is described as

$$E = E_0 \cos(2\pi v_0 t)$$
 (eq. 2.4),

where E_0 is the maximum field strength and v_0 is the frequency of the photon, Equation 2.2 then becomes

$$P = \alpha E_0 \cos(2\pi v_0 t)$$
 (eq. 2.5).

Substituting the polarisability in Equation 2.4, the strength of the induced dipole becomes

$$P = \alpha_0 E_0 \cos(2\pi\nu_0 t) + E_0 Q \left(\frac{\delta\alpha}{\delta Q}\right) \frac{\cos 2\pi t (\nu_0 + \nu) + \cos 2\pi (\nu_0 - \nu)}{2} \quad (\text{eq. 2.6}).$$

Equation 2.6 highlights that the polarisability and scattering intensities have a linear relationship with the incoming light intensity. The equation also shows how Raman scattering will only occur when the polarisability is changed ($\frac{\delta \alpha}{\delta Q} \neq 0$). However, α_0 is more dominant than this change in polarisability, resulting in Rayleigh scattering occurring much more often than Raman scattering, hence one in every $10^6 - 10^8$ scattered photons is scattered inelastically. Furthermore, the change in polarisability over the displacement will fluctuate significantly across different molecules and vibration modes within a molecule. For more complex molecules (a higher number of atoms/bonds) the possible vibration modes that may be affected can be analysed through group theory: an algebraic method which models the properties and behaviour of groups of molecules, resulting in a prediction of the molecule vibrations and hence expected Raman spectrum (Horn 2011).

The intensity of the scattered Raman light is defined as (McCreery 2005)

$$I = K l \alpha^2 \nu^4 \qquad \text{(eq. 2.7),}$$

where *K* comprises a number of constants and *l* is the power of the laser used to induce Raman scattering on a target material. Equation 2.7 signifies how the intensity of the Raman scatter can be governed by the intensity (*l*) and frequency (*v*) of the incoming light, and also from the polarisability, α , exhibited by the target molecules. The intensity is also described as (McCreery 2005)

$$I = I_0 \sigma_i D \, dz \qquad (\text{eq. 2.8}),$$

where I_0 is the intensity of the incoming light, D is the number density of scatterers (molecules/cm³), dz is the path length of the incident light in the sample, and σ_j is the Raman cross-section of a Raman band j (units cm³/molecule). The cross section is defined as the probability of the incoming light inelastically scattering off the target material. The scattered photon will have a particular shift relating to a particular vibration which results in the scattered Raman light being observed as narrow wavelength bands (in comparison to fluorescence emission, which produces a continuum).

The description above assumes that there is no energy absorption from the incoming photon into the molecule. However, this is not normally the case. When specific energies of the incoming photon equate to the binding energies within the molecules, the energy will cause an electron to transition to a higher electron state, resulting in an outer electron transitioning to the lower state, filling the vacancy. The transition of the second electron causes emission of a certain energy. This process is known as fluorescence, a process that can complicate the determination of the intensity and wavenumber of the Raman scattered photons due to the energies involved (relative to those involved in Raman scattering). Notably, the timescales for fluorescence to occur range from 10⁻⁹ to 10⁻⁶ seconds, whereas the Raman scattering timescales are of order 10⁻¹² seconds, a characteristic that can be utilised in the design of an instrument in order to reduce the effects of fluorescence (Misra et al. 2005).

If the frequency of the incoming light equates (at least closely) to the electronic transitions in the molecule, the scattering intensity can significantly increase, an effect known as the Resonance Raman Effect (Robert 2009). Typically, scattering is enhanced by an order of 10³ or 10⁴ (Howell G. M. Edwards et al. 2010) but 10⁶ has also been observed (Smith & Dent 2005).

The shift of energy is measured in wavenumbers, which is defined as

$$\overline{\omega} = \frac{v}{c} = \frac{1}{\lambda}$$
 (eq. 2.9),

where v and λ are the frequency and wavelength respectively of the incoming light, and c is the speed of light, with the units cm⁻¹, and the wavenumber offsets can be converted to the incident light frequency and emitted light frequency through:

$$\overline{\omega} = \frac{\nu_0 - \nu}{100} = \frac{\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}{100}$$
 (eq. 2.10),

where v and v_0 are the frequencies of the scattered and incoming photons respectively, and λ and λ_0 are the respective wavelengths. An example Raman spectrum is shown in Figure 2.3; it shows a calibrated beta-carotene sample acquired using the RLS prototype instrument (described in Section 2.1.4).



Figure 2.3: A Raman spectrum of beta-carotene acquired using the RLS prototype instrument.

2.1.2 Raman Spectroscopy in the Search for Life

Although a Raman spectrometer has not yet been deployed on a space mission (due to availability and technical readiness of necessary instrumentation components), Raman spectroscopy is undoubtedly a high priority technique for searching for biomarkers, organics, and other signs of life processes. The optimum method for demonstrating the analytical technique's ability to identify life signatures (for missions to Mars, Europa, Enceladus, and so forth) is by performing analyses on terrestrial samples that are known to be composed of similar materials and have undergone the same types of processes.

In particular, resonance Raman has been demonstrated to be a potentially effective method for the identification of materials associated with life processes (Marshall et al. 2007; Storrie-Lombardi et al. 2001; Tarcea et al. 2007). Storrie-Lombardi et al. (2001) and Tarcea et al. (2007) showed that excitation by UV light produces strong Raman bands from proteins and DNA/RNA. Marshall et al. (2007) also utilised resonance Raman as a powerful tool to identify chromophore carotenoid

molecules, specifically analysing samples from a harsh environment (hypersaline). They argued that the technique is invaluable as it can identify such material without the need for large sample sizes or complex extraction of the material (that other techniques typically require) (Marshall et al. 2007).

Raman spectroscopy has also been demonstrated to be useful for the identification and characterisation of carbon structures, as well as graphitic and carbonaceous materials (Dresselhaus & Dresselhaus 1982; Marshall et al. 2010). Jehlička & Beny (1999) detail the technique's capability of characterising the structural order and ability to identify carbonaceous matter of structural defects (and note that it is advantageous to complement the Raman analysis with images of the sample through complementary Transmission Electron Microscopy data, for example). Moreover, Jehlička & Bény (1992) demonstrated the possibility of using the technique to identify the chemical structure evolution of a number of kerogen samples; and Khatibi et al. (2018) showed the ability of detecting the molecular alterations of kerogen in organic matter.

As discussed in Chapter 1, Raman spectroscopy has also successfully been used to identify biomolecules that various microorganisms produce in order to survive in harsh environments. Some of the bodies in the Solar System have environments that may not be suitable to support life (for example the high proton radiation environment on Europa, a potentially hypersaline Europan ocean, or the UV radiation on the dry Martian surface). However, the Raman technique is sensitive to the pigments that organisms produce to enable them to survive within the environment, and are able to identify biomolecules, such as parietin and scytonemin. Malherbe et al. (2017) demonstrated the identification of carotenoid pigments on a gypsum sample from a hypersaline lake in Eilat, Israel. Both 532nm and 785nm lasers were used to excite the Raman signal: the gypsum was identified using both wavelengths but the carotenoids (the pigment biomarkers used for protection of the bacteria from the harsh salt environment) were detected with the 532nm laser only. Edwards et al. (2005) reported on the identification of key biomarkers on samples from the Antarctic, providing information about the bioorganic modification of geological strata. Specifically, lichens (colonisers of extreme terrestrial environments) and cyanobacteria, both key biomolecular marks in the search for

extant or extinct life, were identified using Fourier-Transform Raman analysis with a 1064nm excitation wavelength. Edwards et al. (2007) have demonstrated how Raman spectroscopy can be used to identify molecular information through analysing samples that exhibit morphological features related to the biological colonisation of rock substrates, acquired from Martian analogue sites. Using both a 1064nm FT-Raman spectrometer and the 514nm/785nm Raman microscope, Edwards et al. (2007) successfully identified biomaterials and minerals predicted to be observed on samples similar to those expected to be present on Mars.

2.1.3 Raman Instrumentation for Space Missions

A typical Raman spectrometer uses a laser (UV, visible, or IR) in order to induce Raman signal from the target material. The laser is chosen because it can provide a large number of monochromatic photons at the sample. There are a number of factors that determine the wavelength of the laser, λ_0 , including:

- the intensity of Raman signal produced at that wavelength for typical target materials (typically UV generates higher intensity Raman signals than IR);
- the possibility of inducing significant fluorescence levels, which may compromise Raman band sensitivity levels (i.e. reduced fluorescence levels occur with IR Raman spectroscopy compared to UV induced spectroscopy);
- the specific science goals of the spectroscopy application (for example, green laser light is optimal for inducing Raman signal from organics; as well as 514nm and 532nm exciting electron transitions with carotenoid molecules, resulting in the resonant Raman effect (see Section 2.1.2 Raman Spectroscopy in the Search for Life));
- the availability of suitable detectors (i.e. that exhibit high quantum efficiencies across the wavelengths of interest);
- possible damage to the sample (as UV light has a higher energy than IR, it is more likely to damage the target).

The laser light is focussed into a spot on the surface of the sample and the scattered Raman light will be collected by optics. Typically, the collection optics will consist of a number of filters to remove unwanted signals, such as elastically scattered laser
light. As the Raman signal is considerably weak in comparison to Rayleigh scattering (1 in every $10^6 - 10^8$ photons is inelastically scattered), current Raman spectrometers are designed such that the laser and collection optics are located very close to (if not in contact with) the sample. The design (for instance, alignment of subsystems) of the Raman instrument may be optimised to increase the number of inelastically scattered photons acquired (by increasing the power of the laser or optimised positioning of the collection optics), and at intensities that allow a large signal to noise ratio and discernible Raman bands.

The collected light is then diffracted into its component wavelengths using a diffraction grating. The form of grating depends on the spectral range expected from the target materials as well as the spectral resolution required to adequately discern the relatively narrow Raman bands typically produced by sample types important for the specific applications (and hence satisfy the specific science goals of the mission).

The diffracted light is imaged by a solid state detector. Typical detectors include charge coupled devices (CCD) or complementary metal-oxide semiconductor (CMOS) devices. The CCD typically has a much higher quantum efficiency and dynamic range (Janesick 2004). However, CMOS devices are inherently more radiation tolerant than CCDs, resulting in a better signal to noise ratio in harsh radiation environments. A full trade-off between the two devices for various mission scenarios is provided in Chapter 3. The diffracted Raman signal (imaged by the detector) is converted into a Raman spectrum (i.e. signal versus wavenumber) and appropriate processing and analysis is performed on the data in order to identify the Raman bands. A schematic identifying the typical components of a Raman spectrometer is shown in Figure 2.3.



Figure 2.3: An example schematic of a Raman spectrometer.

A Raman spectrometer has yet to be flown on a space mission due to the availability of appropriate lasers and optics that can be utilised in an instrument onboard a spacecraft. The availability of the subsystems necessary to overcome the harsh environments in space, or the reliability of components that will ensure the instrument can operate in an autonomous process.

While no spectrometer has yet been deployed on a space mission, three are planned for launch in 2020. The RLS instrument (Rull et al. 2017) will be the first to launch (on ESA's ExoMars rover), followed by two Raman spectrometers on NASA's Mars 2020 mission SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (Beegle et al. 2015)) and SuperCam (Maurice et al. 2016)). The RLS and SuperCam instruments will utilise a 532nm excitation source, whilst SHERLOC incorporates a UV wavelength laser. Other Raman spectrometers have also been proposed for Martian missions, including the Mars Microbeam Raman Spectrometer (MMRS) (Wei et al. 2015; Wang et al. 2003) and the Compact Integrated Raman Spectrometer (CIRS) (Wang et al. 2014; Wang, J. Lambert, et al. 2016), the latter has also been proposed for a NASA mission to Venus (Wang et al. 2015). The MMRS and CIRS designs have also been considered for missions to the Moon. All of these instruments are described in detail in the Sections 2.1.3.1 to 2.1.3.6.

A Raman spectrometer has recently been proposed for a lander on Europa: the Dual Wavelength Raman/Fluorescence spectrometer (DWARF). DWARF has been developed by JPL and Washington University (in collaboration with the University of Leicester, UK) and is based on two previous spectrometer designs: MMRS and CIRS, both of which have been used in successful field test campaigns (Wei et al. 2015; Wang et al. 2014; Wang, J. Lambert, et al. 2016).

2.1.3.1 MMRS

The MMRS is designed with an arm mounted optical probe coupled to a low mass spectrometer via an optical fibre (Wei et al. 2015; Wang, J. Lambert, et al. 2016). The instrument comprises two key sub-system units. The first is an optical probe with a 532nm laser for Raman excitation. The probe utilises a stepper-motor mechanism enabling a ~1cm line scan over the target sample. The second unit incorporates an 808nm diode pumped laser to power the probe, the optics and detector for collection of the Raman scattered light, a calibration lamp, and respective electronics and microprocessors. The probe can be fixed onto a rover arm or carousel to perform in-situ analysis of the samples, and is then connected to the main unit by 2 optical fibres. It can be operated up to 10mm from the sample, producing a focussed laser spot with a power of 20-30mW and a diameter of <20 μ m. A schematic of the instrument is shown in Figure 2.4. The diagram shows the path of the light through the instrument, and the relative positions of the components; it also shows the probe being pushed against the sample for analysis.



Figure 2.4: A schematic of the MMRS with the probe, spectrograph, and ancillary units (Wang et al., 2003).

The MMRS spectral range is 100 – 4000cm⁻¹ (specifically: 200-1800cm⁻¹ for mineral and graphitic carbon characterisation; and 2500-4000m⁻¹ for detection of water and the organic functional group (Wang et al. 2003)), and has a spectral resolution of 7-8cm⁻¹ (Wei et al. 2015). The MMRS instrument has been utilised during three separate field tests in the Atacama Desert, twice on the Zoe rover, and once standalone (Wang, J. Lambert, et al. 2016). During the field tests, the instrument has successfully identified a variety of igneous materials, carbonates, sulphates, and carbonaceous materials in such environments (Wei et al. 2015). MMRS was proposed for the MSL mission and, although it was not selected, was reported as capable and classified as 'Category 1' (Sharma & Wang 2007).

2.1.3.2 CIRS

Building on the heritage and design of the MMRS instrument, the Compact Integrated Raman Spectrometer (CIRS) (Figure 2.5) instrument was designed for future space exploration opportunities (Lambert et al. 2014; Wang, J. Lambert, et al. 2016). The key areas of development/variation from the MMRS instrument are: CIRS is a non-optical-fibre version of MMRS; CIRS combines the Raman spectrometer with a context imager. The inclusion of the optical head located directly on the spectrometer allows for an increased Raman signal strength (Wang et al. (2014) found an overall Raman signal improvement of 20%). The context imager replaced the mirror in the MMRS design, allowing for a 3 x 12mm image of the target sample to be acquired in parallel to the acquisition of a Raman spectrum, providing greater context for the analysis (Wang et al. 2014). The imager has a field of view of approximately 37 x 26mm and a chip format of 1600 x 1200 pixels (Wang, J. Lambert, et al. 2016). A further addition to the CIRS instrument is the inclusion of 3 UV LEDs (250nm or 280nm) that can be used to excite the sample thereby generating UV-stimulated fluorescence (this technique was successfully tested in the Atacama Desert) (Wang et al. 2014). Another addition was the ability to perform Shifted Excitation Raman Difference Spectroscopy (SERDS) or Sequential Shifted Excitation Spectroscopy (SSES), which can be used to separate the molecular information contained in the Raman bands from the fluorescence (Lambert et al. 2014).



Figure 2.5: Inside the CIRS instrument, developed by JPL and Washington University (Wang et al., 2014).

The excitation source is a Diode Pumped Solid State (DPSS) laser emitting at a wavelength of 532nm. With a power range of 0.5-50mW, the laser spot is focussed to a diameter of 37.5 μ m. The CIRS spectral range is 183 – 4432cm⁻¹ and its spectral resolution is 9cm⁻¹ (Wang, J. Lambert, et al. 2016). The detector used for acquiring the dispersed Raman signal is an inverted mode, frame transfer CCD47-20 detector (1024 x 1024, 13 μ m pixels). For the typical Raman spectral range, the device has a quantum efficiency of >90%, a full well capacity of ~100,000 electrons, and the system can achieve a dynamic range of 10,000:1 (e2v Technologies 2017a).

The CIRS instrument was first designed as a Raman spectroscopy instrument that was proposed for NASA's Mars 2020 rover mission(Wang et al. 2014), and was also considered for a potential mission to Venus, led by NASA (Wang et al. 2015).

2.1.3.3 DWARF

The Dual Wavelength Raman system (DWARF) is a further evolution of the CIRS and MMRS instruments (Wang et al. 2018). The development programme will result in a TRL6 instrument, relevant to / designed for landed missions to the icy moons of giant planets, such as Europa. DWARF is a Dual Wavelength Raman/Fluorescence spectrometer, designed to enable the identification of a number of planetary materials using Raman spectroscopy, while simultaneously performing laser induced fluorescence (LIF) analysis in order to characterise low levels of organics and some trace minerals (Wang et al. 2018).

The proposed design implements an additional excitation channel, a 785nm laser, which will share the path of the main optics, detector, and electronics utilised by the 532nm system. Environmental tests (focussing on radiation tests representative of the Europan environment) will be performed on the full system, and the results will help to guide the final optimised design of the instrument (for example, after analysing which detector can still meet the science requirements when operated in a high radiation environment).

2.1.3.4 RLS

The Raman Laser Spectrometer (RLS) is an instrument in the ExoMars ALD onboard the ExoMars rover. It will be used to analyse the molecular composition of the material extracted from the subsurface by the rover's drill (the samples will be crushed into powder with an average grain size of 200-250µm by the sample preparation system onboard the rover (Vago et al. 2017)). The instrument is likely to be the first Raman spectrometer flown in space. The scientific requirements for RLS are (Rull et al. 2017):

- 1. To identify organic compounds and search for life;
- 2. To identify mineral products and indicators of biologic activity;
- 3. To characterise mineral phases produced by water related processes;
- 4. To characterise igneous minerals and their alteration products;
- 5. To characterise the water/geochemical environment as a function of depth in the shallow subsurface.

The RLS instrument was first proposed in 2003 as EXLIBRIS (Maurice & Rull 2003). EXLIBRIS was designed as a combined Raman-LIBS (Laser Induced Breakdown Spectroscopy) spectrometer located on a mast (which would provide movement of the instrument to up to 2.5m away from the rover) and utilising an ND:YAG pulsed laser (ESAPB_HME 2009). As with the current design, the instrument was proposed to be positioned in contact with the target sample; however, in the original proposal the instrument analysed material from the rover's arm (for surface analysis) as well as inside the ALD (i.e. in order to analyse the drill samples). In 2005, the design was adapted in order to remove the rover arm functionality following a descope of the rover (i.e. measurements performed only inside the rover).

The current design of the RLS instrument includes a spectrometer unit (SPU), pictured in Figure 2.6, an optical head unit (iOH), and the electronics control unit (ICEU). A number of key trade-offs were performed for the optimisation of the instrument, with regards to the science and engineering goals of the instrument/mission (Rull et al. 2017): i.e. the wavelength of the excitation laser, and the design of the spectrometer unit.



Figure 2.6: The engineering and qualification model of the RLS SPU (Rull et al., 2017).

The laser wavelength for the RLS instrument was chosen for the following reasons. Despite the efficiency in inducing fluorescence at this wavelength, a green laser is approximately 20 times more effective at inducing Raman scattering than a NIR laser (specifically, it has been found that in the spectral range 0 - 4000cm⁻¹, excitation by a laser in the visible range produces intensities 60 times greater than those excited by an IR laser (Edwards & Chalmers 2005)). This significant intensity increase is of particular importance for the ExoMars science goals in which the RLS instrument will be used to identify CH and OH groups (which appear in the range 2800 – 3650cm⁻¹) (Rull et al. 2017). Another key aspect in the selection of laser wavelength for the instrument is the detection efficiency: the detector used has a higher quantum efficiency at visible wavelengths, significantly dropping off at both the UV and NIR wavelengths (unless specifically designed for a wavelength range; described in detail in Chapter 3).

Another important consideration during the design of the RLS instrument was the number of moving parts (i.e. in order to decrease the risk of failure). Given this constraint, it was concluded that the spectrometer should be designed around a transmission holographic grating concept. In this design, the spectral resolution of the instrument is independent of the focal length, resulting in a more compact system (Dubessy et al. 2012; Rull et al. 2017).

The final design incorporated (Rull et al. 2017) the iOH, focusing the 532nm laser light onto the powdered sample with a spot diameter of ~50 μ m. The scattered Raman signal will be collected by the iOH via a separate set of filters and optical components (i.e. those used for excitation), in order to remove unwanted signal (i.e. background ambient light/Rayleigh scattering). Furthermore, the iOH has been designed with a focussing mechanism, allowing fine adjustment in steps of ±1mm, resulting in a spatial resolution of ±2 μ m. The collected Raman scattered signal is then transmitted through optical fibres to the SPU. The SPU unit utilises a holographic grating transmission spectrograph, which is used to disperse the Raman signal (from the powdered drill cores) onto a full frame, back illuminated CCD (with 2048 x 512, 15 μ m pixels). The grating (1800 lines/mm) produces a spectral resolution of between 6 and 8 cm⁻¹ in the optical range 533 to 676nm. During the mission, dark current noise and electronics noise will be reduced through the implementation of a thermoelectric cooler (TEC) connected to the detector, operating the RLS instrument within the temperature range -10°C to -40°.

Before launch, the RLS instrument will undergo a number of experimental campaigns in order to verify and optimise performance when analysing materials likely to be acquired by the drill core. As the instrument will be the first to perform in-situ analysis on Mars, the performance characterisation demonstrations have utilised analogue sample materials similar to those found in Martian meteorites and on locations on Earth similar environmentally to that on Mars (i.e. locations which exhibit similar geological process and have similar harsh environments, which affect the geology). Specifically, the campaigns have focussed on the instrument's ability to identify molecules linked to hydration states and the processes involved in a hydrological cycle. Successful field tests have been performed at analogue sites which include: Rio Tinto, Jaroso Ravine, and Tenerife (Rull et al. 2017) and in the Utah desert (funded and organised by the UKSA) (Balme, in review), as well as successful laboratory simulations (Lopez-Reyes et al. 2012; Lopez-Reyes et al. 2013).

2.1.3.5 SuperCam

The SuperCam instrument onboard NASA's Mars2020 rover consists of a suite of 5 instruments that provide complementary data in the form of: Raman spectroscopy, LIBS, time-resolved fluorescence, Vis-NIR spectroscopy, and high resolution microimaging. The science goals of the instrument are (Maurice et al. 2016):

- 1. To perform the mineral, chemical and textural characterisation of rocks;
- 2. To characterise the texture and composition of the sedimentary structures;
- 3. To analyse astrobiologically relevant materials and determine the best location for contact science;
- 4. To constrain the aqueous processes involving volatiles and provide data on volatile content;
- 5. To acquire high resolution colour images in order to obtain detailed information on dust covering, target morphology and texture;
- 6. To analyse coatings allowing identification of late-stage weathering and its relationship (if any) to biological activity;
- 7. To investigate the soil potential for biosignature preservation
- 8. To characterise atmospheric molecules, water ice, and dust.

SuperCam was based on the ChemCam instrument that was developed for the MSL rover. The Raman instrument in the SuperCam suite, utilises a 532nm laser and its spectrometer replaces one of the ChemCam reflection spectrometers within the main unit (Wiens et al. 2016). Furthermore, a significant difference between the RLS and SuperCam instruments is that the latter focusses on inducing Raman scattering on a target at a distance of up to 12m from the rover (with a field of view of 0.65mrad and 1.3mm at a 2m distance) (Wiens et al. 2016). The aim is to achieve stand-off Raman spectroscopy with the use of an intensifier on the detector, that gates within 100ns of the laser pulses. The gating is designed to reduce the effects of fluorescence produced by the sample as well as ambient martian light (Wiens et al. 2005). Utilising the time difference between acquisition and the laser pulse facilitates time resolved fluorescence analysis (Sharma 2007). The stand-off Raman technique is particularly complementary to the information obtained using Vis-NIR spectroscopy (Wiens et al. 2016), since Raman bands are often not detectable with

Vis-NIR, resulting in identification of samples such as feldspars (an expected material at both Mars 2020 landing sites) (Wiens et al. 2016).

2.1.3.6 SHERLOC

The second Raman spectrometer that will be included on the Mars2020 rover is the SHERLOC instrument, a deep UV native fluorescence and Raman spectrometer (Beegle et al. 2015). The instrument will be mounted on the arm of the Mars 2020 rover and will utilise a 248.6nm laser (Beegle et al. 2016). The DUV wavelength was chosen to excite fluorescence from the sample, specifically targeting carbon and organic molecules (fluorescence of organics extends from ~270nm into the visible wavelength (Beegle et al. 2016)). Aromatic organic compounds can be identified by fluorescence as the cross-section is typically 10⁴ larger than that of Raman (Beegle et al. 2016). The Raman spectroscopy will be used to provide additional molecular information on the aromatics and aliphatic organics and minerals (Beegle et al. 2014).

The instrument will be used in conjunction with a context imager to autofocus and scan the sample, combining spectral information with morphological and textural information (Beegle et al. 2016). The laser will be focussed on a spot of diameter 100m, scanning a target area of 7x7mm.

2.1.4 Instrumentation for the Search for Life

As described in Section 2.1.2, Raman spectroscopy is an ideal analytical technique in searching for signs of life on other bodies in the Solar System. A number of Raman spectrometer designs are considered, trade-offs are performed for each, and the final designs are characterised, all with regards to the search for life. The instruments are DWARF, the RLS prototype, and a 785nm handheld Raman spectrometer. DWARF was described above; the latter two are described below.

An RLS prototype has been developed as a bench-top, flight representative Raman spectrometer at the University of Leicester. It was produced for performance testing and analogue sample characterisation campaigns for the ExoMars rover mission. Each component in the spectrometer has been selected based on a number of tradeoffs to help guide and enhance the design of the RLS instrument, so that it can be optimised to acquire the data necessary to satisfy the science goals. The laser produces a 532nm spot (the diameter can be altered between 50µm and 150µm) with a power of 100mW. The scattered Raman signal is collected by a Kaiser optical head (which encompasses a notch filter) and transmitted through a set of fibre optics to a Kaiser Optical HoloSpec spectrograph. The dispersed Raman signal is then collimated onto and imaged by a CCD detector (e.g. CCD42-10). The spectral range of the prototype is 200cm⁻¹ to 4000cm⁻¹ and its spectral resolution is approximately 3cm⁻¹. An image of the prototype is shown in Figure 2.7.



Figure 2.7: The RLS prototype developed by the University of Leicester.

Another representative Raman spectrometer used in this work is the DeltaNu Inspector Raman instrument, utilising a 785nm NIR laser. The laser can achieve a power output of 120mW and can produce a spot of diameter 75µm. In the spectral range 100cm⁻¹ to 2000cm⁻¹ the resolution is <8cm⁻¹.

2.2 UV AND VISIBLE SPECTROSCOPY

2.2.1 UV-Vis Spectroscopy Theory

When UV or visible light (with a frequency similar to the transition frequency of the atoms/molecules present in the target material), is incident on a sample, the

electrons absorb the energy of the incoming photon, exciting them to an excited state. Such absorption results in a fraction of the incident light being transmitted through the material (Figure 2.8). The absorption (which is specifically related to the analyte's concentration) is determined by comparing the initial intensity, *I*₀, to the measured power, *I*. A full profile of the absorption can be recorded across the wavelength range (a background profile must also be taken as absorption can occur without presence of the analyte).

Measuring the intensity between the incident light and the transmitted light can reveal significant molecular information about the sample. The molecular information arises due to the fact that the transition frequencies in the material are unique to the molecules present in it. Hence, a measure of the transmitted intensity/amount of absorption for each wavelength is unique to each material. That is, the resultant transmitted intensity/absorption spectrum can be classified as the fingerprint of a particular material. Furthermore, performing the absorption spectroscopy on samples with known substances allows for an analysis of the concentration of material in the sample versus the amount of light absorbed.



Figure 2.8: A diagram demonstrating incident light being absorbed through a material, with the resultant intensity providing information about the material.

The absorbance through a material at a given wavelength, A_{λ} , is given by

$$A_{\lambda} = \log_{10} \left(\frac{I_0}{I} \right) \qquad \text{(eq. 2.11)}.$$

It is possible to analyse the concentration of the sample as a function of absorbance, defined by

$$A_{\lambda} = \varepsilon_{\lambda} lc$$
 (eq. 2.12),

where ε_{λ} is the wavelength dependent molar absorptivity coefficient, *l* is the path length of the light through the material, and *c* is the analyte concentration.

2.2.2 UV-Vis Spectroscopy in the Search for Life

UV-vis absorbance and fluorescence spectroscopy can be utilised in the search for life to identify organic and inorganic compounds, as well as detect microbial activity through fluorescence. Birdwell & Engel (2010) identified strong microbial fluorescence features from thermal spring waters in a sulfidic cave system. This could be employed in space exploration to identify potential life in surface and subsurface lakes/oceans (such as those on Europa/Enceladus).

2.2.3 UV-Vis Instrumentation

A UV-Vis spectrometer will use 1 or 2 broadband light sources (the number will depend on the wavelength range required for spectroscopic analysis and the range the lamp produces), typically a Deuterium lamp or Halogen lamp. The light is focussed on a concave mirror and angled towards a monochromator. The monochromator is used to refract the light into specific wavelengths illuminating the sample. The monochromator is usually motorised such that it can step through the wavelength range required.

A beam splitter is positioned between the monochromator and target sample, allowing 50% transmission through to the sample and 50% reflect to a mirror which is focussed onto a reference sample. The reference sample is used to measure the initial intensity of the beam of light, *Io*. Both sources of light are acquired by a detector, specifically designed to have a higher quantum efficiency in the wavelength range of interest. The data is then processed to calculate the absorbance through the target material at each wavelength and a spectrum can be generated of absorbance (or transmitted intensity) against wavelength. A schematic of a UV-Vis spectrometer is shown in Figure 2.9.



Figure 2.9: A schematic of a UV-Vis spectrometer.

The UV-Vis spectrometer used in this thesis is the Lot-Quantum Design Xenon lamp in conjunction with a 150mm focal length monochromator. The lamp and monochromator can output a continuous wavelength range of 250nm to 2400nm. The monochromator can be used with two slits of sizes $10\mu m$ and 3mm. A UV spectrum of food colouring is shown in Figure 2.10 as an example spectrum that can be acquired.



Figure 2.10: A UV spectrum of red food colouring (credit: Dr D Kennepohl).

2.3 X-RAY FLUORESCENCE

2.3.1 XRF Theory

If the energy of an incoming photon corresponds to the energy gap between the ground state of the element and the binding energy of the shell, an electron on the respective shell will absorb the energy and be promoted to an outer shell (if the incoming photon has sufficient energy it can cause the electron to undergo photoionisation). A secondary electron will transition to the original shell to fill the vacancy, emitting a secondary X-ray equal to the energy difference between the two shells. Acquisition of the secondary X-rays (after a high number of interactions) results in an energy spectrum specific to the target material. The process described is known as X-ray Fluorescence (XRF). An energy spectrum of lead is provided in Figure 2.10 as an example spectrum acquired through XRF spectroscopy.



Figure 2.10: An energy spectrum of lead.

The structure of an element is described by the Bohr model, shown in Figure 2.11 for silicon. The Bohr model describes the atom as a positively charged nucleus orbited by the shell electrons. The shells are labelled in the figure using X-ray notation: i.e. the first shell is K, the second shell is L, and so on. The promotion of the electrons from the inner shells (most typically the K shell) is due to the absorption of the incoming X-ray energy, transition of an electron from an outer shell that cause

XRF. The energy required to cause electron transitions from the outer shells is only a few eV, hence requires the light from the visible part of the spectrum to cause such transitions. However, electrons in the inner shells experience a much stronger attraction with (and are not well shielded from the element's nuclear charge). The energy required to overcome the force the electrons experience is of the order a few keV; hence interactions with X-rays cause such transitions. The most common transitions in XRF are illustrated in Figure 2.12.



Figure 2.11: An example of the Bohr model of silicon, showing the layout of electrons on the K, L, and M shells, which orbit the nucleus.



Figure 2.12: An example of the electron transitions for the first four inner shells of an atom, with their corresponding notation.

The change in energy between the two shells involved is discrete and specific to the transition (as it is associated with the binding energies of the shells). Each element exhibits a specific, unique set of binding energies and hence the resultant measured spectra are characteristic to the element; the spectrum is essentially a fingerprint of the element (similar to the unique absorption spectra in UV-Vis spectroscopy).

2.3.2 XRF in the Search for Life

When utilised for space missions, XRF is typically included in an Alpha Particle Xray Spectrometer (APXS) instrument (these have been flown on a large number of missions, as described in Section 2.3.3 APXS Instrumentation). The APXS instrument utilises 3 different types of interaction with the elements in the target sample: Rutherford backscattering (alpha mode), nuclear reactions with light elements (proton mode), and generation of characteristic X-rays through ionisation by alpha particles (X-ray mode). In the alpha mode, the instrument can detect all elements heavier than Helium, and acquires the most intense signal/is optimum for Carbon, Nitrogen, and Oxygen, whilst acquiring the lowest signal for elements heavier than Silicon. The X-ray mode is sensitive to elements heavier than Sodium, increasing in resolution with heavier elements. Typically, the alpha and X-rays modes are included; the proton mode is used for complementary data obtained in the transition region (Na, Mg, Al, Si). The instrument can measure abundances of all elements except H and He (Rieder et al. 1977).

An XRF instrument would provide invaluable complementary data if it was included along with a Raman or UV-Vis spectrometer, particularly onboard a mission to Europa or Phobos and Deimos. Currently, little is known about the composition of the three moons and identifying the elemental abundances will provide a much more detailed understanding of the origins of the moons and current geological processes. Retrieving this information is invaluable for the search for life: understanding the geological context of the environment (in which, for example, the Raman spectrometer is deployed to search for molecular signs of life) can help provide confidence that the location can support life processes, providing a confidence (or otherwise) for the data acquired by the molecular spectrometer.

2.3.3 APXS Instrumentation

An APXS instrument consists of a radioactive source, which irradiates the sample with X-rays and alpha particles. Typically, the radioactive source Curium-244 is used, which emits alpha particles of energy 5.8Mev, and X-rays are emitted from the decay of Plutonium-240 (with energies 14keV and 18keV). The scattered alpha particles and secondary X-rays emitted from the sample are collected by a detector positioned directly over the sample. An example schematic of an APXS instrument is shown in Figure 2.13.



Figure 2.13: A schematic of a typical APXS instrument. The left shows the side view, the right shows the front view. This schematic is based on the Rosetta APXS.

XRF spectroscopy is relatively insensitive to surface roughness and the measurement geometry does not need to be known accurately. However, as discussed in the previous section, XRF alone can only identify a limited number of materials (hence why the alpha and proton modes are included as complementary data). It is also necessary to optimise the alpha and X-ray detectors to have a quantum efficiency in the energy range expected to be acquired in the mission. As described in the next chapter, there are certain architectural modifications that should be made to the detector to enhance its capabilities for certain energies ranges, including deep depletion or back illumination.

2.3.3.1 APXS in Space Missions

The first APXS was proposed for the Viking missions (although the three Surveyor missions in 1960s included an APS – the instrument with the alpha and proton modes, but without XRF). However, the first flown APXS (which included the proton mode) was on Sojourner, as part of the Mars Pathfinder programme (Rieder et al. 1997b). The aim of the instrument was to characterise the geology of the landing site. By identifying the relative amount of iron and magnesium versus the silica in the soil, analysis of data returned from the instrument determined that the area,

known as Barnacle Bill, was analogous to Earth's andesites, confirming Mars had been through a volcanic period in its history. The Sojourner APXS was the first of a series of such instruments to be used on Mars, with a miniaturised design (low mass and power consumption); hence ideal for in-situ analysis (Golombek et al. 1999).

Although the Philae comet lander reached its target after the MER programme reached Mars, the APXS instrument onboard Philae was designed and built before that on MER and was the Martian rover's predecessor (Klingelhöfer et al. 2007). The Rosetta instrument was an enhancement of Sojourner's as it included a silicon drift detector for higher energy resolution when acquiring the X-rays. The Philae AXPS was designed specifically for deployment on a comet: it had a dedicated positioning device which lowered the sensor head to the surface of the comet. Moreover, it was optimised to operate in an extreme variable temperature environment (Klingelhöfer et al. 2007).

The APXS instrument on the MER mission was mounted on the rover arm (the instrument deployment device). The instrument shown in Figure 2.14, was designed to determine the chemistry of crustal rocks and soils, as well as to analyse the water-related deposits, sediments, or evaporates at the landing site region (Rieder et al. 2003). The instrument design optimised the Pathfinder APXS coaxial arrangement of radioactive sources and detectors, implementing a higher efficiency detector; including a titanium foil over the alpha sources and preamplifiers for the detectors in the sensor head; and operating a protective door for the calibration target (Rieder et al. 2003). The detector used for XRF analysis improved the sensitivity to elements from Ca to Fe by a factor of 10, and enable instrument acquisition times to less than 10 minutes.

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Figure 2.14: The APXS on the MER mission (credit: NASA/JPL-Caltech).

Currently, the MSL rover Curiosity deploys an APXS instrument (the instrument onboard Opportunity rover is still running, to date). A significant improvement from the MER instrument is that the Curiosity APXS can perform a full chemical analysis a factor of 3 times faster. Moreover, the instrument was designed to operate at temperatures as warm as 5°C, whereas the MER APXS could operate most efficiently at -40°C (Gellert et al. 2009). The instrument can identify elements from Na to Br and beyond, with a sensitivity improvement of a factor of 3 compared to the MER instrument (Gellert et al. 2009).

The next APXS instrument to be launched will be onboard the Chandrayaan-2 rover, in late 2018. The aim of the instrument is to analyse the soil and rock samples acquired from the rover track, identifying major elemental compositions in the high latitude polar regions of the moon (Shanmugam et al. 2014). It is designed as a single package carrying the ²⁴⁴Cm radioactive source, generating both the alpha and X-ray modes, identifying elements from Na to Br.

Chapter 3

Camera System Functionality and Characteristics

3.1 INTRODUCTION

In this chapter, two types of solid-state detector that are suitable for space applications (the charge-coupled device and the complementary metal-oxidesemiconductor detector) are described. Specifically, their overall scientific performance, operation, structure, and fundamental characteristics are compared.

3.2 CHARGE-COUPLED DEVICES (CCD)

3.2.1 Charge Generation

The charge coupled device (CCD) was first conceptualised at the Bell Telephone Laboratories by Boyle & Smith (1970). The detector consists of an array of coupled capacitors usually made of silicon. When a bias is applied to the electrodes on the surface, a potential well forms in a depletion region below the electrodes in the silicon substrate. The charge from the incoming photons collects in these local minima of potential and is then transferred down the device by varying the bias across the overlying electrodes. The process is as follows, and is represented in Figure 3.1:

i. Incoming signal is converted into an electron in the silicon via the photoelectric effect, followed by various collisional processes forming clouds of charge. This process differs slightly depending on the wavelength of the incoming light. When the signal is in the UV-optical-IR range (for instance, diffracted Raman light or UV absorption), the photon interacts with the silicon atom. If the energy imparted from the incoming photon is large

enough to overcome the bandgap energy of the material (in silicon this energy (1.1eV) equates to photon wavelengths which are smaller than 1 μ m) an electron will be promoted from the valence band to the conduction band, resulting in one free electron being photoionised per photon. In this case, the quantum efficiency of the device (the fraction of incoming light converted into electrons, i.e. measured signal) will be determined by whether the energy of the incoming photon is large enough to pass through the front of the device and to overcome the bandgap energy of silicon, but not so high that it is likely to travel through the device. It will also depend on whether the single electron photoionised by the photon is collected and transferred efficiently through the device.

However, if the incoming radiation has an energy that is equal to or greater than the energy required to generate an electron-hole pair in silicon (3.65eV) (e.g. an X-ray), there will be enough energy in the interaction between the incoming photon and the silicon atom to cause a cascade effect: the photon and freed electrons will continue to cause the photoionization of a number of atoms until the energy is too low to do so. In all cases, the result is a cloud of electrons that is proportional in size to the original signal.

Most of the charge clouds are collected in potential wells (pixels) in the ii. **depletion region of the detector.** The device incorporates electrodes which define the pixel structure of the detector. When a bias is applied to these electrodes, labelled as V_q (gate voltage) in Figure 3.1, an electric field forms beneath them (in the depletion region) creating separated potential wells. The potential wells are constrained by channel stops on either side of the electrodes, causing the voltage (and hence electric field) to reduce to 0. This spatially separated potential well is known as a pixel, the size of which is determined by the format and number of electrodes. The electrons generated in step 1 are attracted towards the nearest potential well, where they are collected. As the potential wells are spatially separated and the electron clouds are collected in the nearest pixel (i.e. assuming generation in the depletion region: if they have been generated in the field free region, the clouds may diffuse over a number of pixels, explained in detail in Section 3.2.2.1) this process enables the position of the incoming signal to be readily determined. The pixels are readout sequentially and with appropriate post processing, the location of each pixel, and hence location of the incoming signal, can be determined.

iii. The charge clouds are clocked towards a register where they are sampled/measured. The electrode biases, V_g , are alternated in order to shift the packets of charge down the device to be sampled. As one electrode is switched to 0V and a bias is applied to the neighbouring electrode, the electrons in the charge packet are attracted to the potential well under the neighbouring electrode. This process, usually referred to as clocking, continues until the charge has been transferred to the output node at the end of the serial register (usually located at the bottom of the device).



Figure 3.1: A basic illustration of the clocking sequence. The incoming signal in part (i) is converted into a cloud of electrons through the photoelectric effect. Parts (ii) and (iii) illustrate the charge cloud being transferred down the CCD by alternating the voltages across neighbouring electrodes, causing the electrons to move potential wells.

A CCD is a semiconductor device. Unlike an insulator, where the gap between the valence and conduction band is too large, the electrons in a semiconductor can transfer across the gap when there is sufficient thermal energy available. For a silicon detector, when an incoming photon has a high enough energy it is absorbed by the silicon crystalline structure. The absorption energy results in an electron in the valence band to be transferred to the conduction band resulting in it becoming a free electron. For a silicon semiconductor, the band gap ~ 1.1 eV, equivalent to a wavelength of 1µm. Therefore, photoionisation will only occur in a silicon detector if a photon has a wavelength less than 1µm.

An important characteristic of the CCD is the probability that the incoming signal will interact with the silicon to cause the promotion of the electron into the conduction band. The attenuation of the intensity of the incoming photon at any distance, *x*, through the silicon is described by

$$I(x) = I_0 e^{-\mu x}$$
 (eq. 3.1),

where I_0 is the initial photon intensity and μ is the linear absorption coefficient. The absorption coefficient is a complex function, dependent on the density and atomic number of the material (in this case, silicon). It is the reciprocal of the absorption length, or the mean free path of the incoming radiation (the depth at which the intensity of the signal has been reduced to 37%).

The particular way the incoming radiation interacts with the silicon depends on the energy of the incident light. Sections 3.2.1.1 and 3.2.1.2 detail how the interaction differs for X-ray and optical photons.

3.2.1.1 X-ray interactions

Once the electron has been transferred to the conduction band an electron-hole (eh) pair is created. If the energy of the incoming photon is high enough, such as is the case for an X-ray, there is a chance that the initial free electron will collide with electrons in the valence bands of other atoms, causing more e-h pairs to form. This is due to the free electron being imparted with a significant kinetic energy:

$$KE_e = E_{ph} - E_b$$
 (eq. 3.2),

where E_{ph} is the energy of the incoming photon and E_b is the binding energy for the electrons in the K-shell of a silicon atom (1.78keV). It is also possible that the energy is sufficiently high that the Auger process occurs, in which two e-h pairs are created. This formation can cause a chain of further Auger processes until the energy is insufficient to create more e-h pairs. The entire process of e-h pair formation results in an electron-hole cloud where the number of pairs created is given by

$$n_e = \frac{E_{ph}}{\omega} \qquad \text{(eq. 3.3),}$$

where E_{ph} is the energy of the incoming photon and ω is the energy required to form an e-h pair. This energy is specific to the material of the detector and the temperature at which the detector is operated (for silicon at room temperature, ω = 3.65 eV per electron). As highlighted in equation 3.3, the number of e-h pairs generated is directly proportional to the energy of the incoming photon. This cloud of e-h pairs is then collected in the pixel potential well, and read out in the manner described in Section 3.2.1.

3.2.1.2 Interaction of Optical Light

Initially, optical photons interact with the silicon in the same way as high energy photons. That is, by promoting an electron into the conduction band via the photoelectric effect. However, in this case when the wavelength of the incoming photon is less than 1μ m, only one electron is released per photon (if the energy of the resultant electron does not have enough energy to ionise more electrons) and hence the number of electrons in a pixel is directly proportional to the intensity of the light.

Another important factor regarding the interaction of optical light with the silicon detector, is the interactions that arise due to reflections and refraction. The optical light (specifically, the fraction that has not yet been absorbed by the material) reflects and refracts at the various boundaries of the CCD's materials/layers (detailed in Section 3.2.2 Device Manufacture and Structure), which results in fringing (also referred to as etaloning) across the CCD. This effect is visible in Figure 3.2 (an image acquired of the fringing that can occur), and is of greatest significance in the red part of the optical spectrum. This phenomenon causes a modification in the quantum efficiency of the detector (the fraction of incoming light absorbed and collected as useful signal). One of the main causes of the fringing is the large difference between the refractive index of air and silicon. A method of overcoming this limitation, and improving the quantum efficiency of an optical CCD is by coating the surface in an anti-reflection (AR) coating. The purpose of this coating is to reduce the refraction across the first boundary (from air to the substrate) by manufacturing a thin film (coating) with a refractive index between that of air (n_0) and the substrate (n_s) , given by the equation

$$n_f = \sqrt{n_0 n_s}$$
 (eq. 3.4).

The effect of the thin film results in a phase shift of 180° between any reflected light at the air-film boundary and film-substrate boundary. The phase shift results in

destructive interference between the refracted light at the two boundaries, reducing the fringing effect. The fringing phenomenon, its effects on the quantum efficiency, and the optimisation through the inclusion of an AR coating are described in more detail in Section 3.2.3.2.



Figure 3.2: Interference fringing in a thin back-illuminated CCD (Waltham 2013).

3.2.2 Device Manufacture and Structure

A CCD comprises a 2D array of closely spaced MOS capacitors. A metal-oxidesemiconductor (MOS) consists of a metal contact, an oxide layer, and a semiconductor. In the case of a CCD, these are the electrode, silicon oxide, and doped epitaxial silicon, respectively (Waltham 2013). There are usually three electrodes per pixel, made from polysilicon that are used to collect the charge in spatially separated regions and transfer them down the device. The electrodes are deposited parallel to one another, and perpendicular to channel stops (a p+ potential barrier implanted in the silicon). These channel stops are used to constrain the potential wells to the boundaries of each pixel in the direction orthogonal to the electrodes, ensuring the charge does not diffuse across different pixels before the transfer process is activated. The silicon oxide layer is located under the electrodes and isolates the silicon layers from the polysilicon electrodes. Often, a silicon nitride (Si₃N₄) layer is included; this layer acts as further insulation and is used to avoid non-uniform growth of the silicon oxide (D Burt et al. 2017).

The p-type silicon forms the active region of the CCD, known as the epitaxial region (formed through the process of epitaxy), and is the location in the CCD where the electron clouds experience the effect of the applied electric field (i.e. within the depletion region) and are collected in the potential wells. When the bias is applied to the electrodes, a depletion region forms in the epitaxial region (the area is depleted of holes), inducing the electric field/potential well. The formation of the depletion region and induction of the electric field is described in detail in Section 3.2.2.1. Currently, CCD devices are mainly being manufactured using buried channel MOS capacitors, in which n-type silicon is implanted into the epitaxial region. This process was significant for the optimisation of the CCD: previously charge was collected at the surface of the CCD at the Si-SiO₂ interface (this type of CCD is specifically known as a surface channel detector (Waltham 2013)). In this type of detector, the electrons can be trapped at the interface and are therefore not always efficiently transferred between pixels (Janesick 2001), substantially degrading the charge transfer efficiency (a characteristic of a detector describing how effectively electrons are transferred across a device (Waltham 2013)). The n-type material is implanted to ensure that electrons are transferred in a region that is some distance away from the interface, reducing the chance of trapping. The epitaxial region is located on top of a (p+ material) silicon substrate, on which the active region is grown. The substrate has a voltage applied across it to ensure that any unwanted charge that may have been photoionised in this region has been removed. An example cross section of a buried channel CCD is shown in Figure 3.3.



Figure 3.3: A cross-section of a buried channel CCD showing the various layers. There are usually 3 electrodes per pixel neighboured by the channel stops to separate the potential wells, forming the pixels. The electrons are collected in the epitaxial region and are kept away from the insulating oxide layer by the buried channel material.

The section of the CCD that is covered by the electrodes described above is called the imaging area, where the electron clouds are generated (from interactions with the incoming photons), collected, and transferred from pixel to pixel. There are typically three electrodes per pixel used to clock the charge to be read out. These imaging clocks are referred to as $I\phi 1$, $I\phi 2$, and $I\phi 3$. The clocks can be sequenced towards switch the electrodes on and off in an order which transfers the charge to the readout register of the device. The typical sequence is shown in Figure 3.4, which illustrates an example of a clocking sequence. Before the first electrode is switched off, the neighbouring electrode must be switched on in order for the charge to begin transferring across. The first electrode is then switched off to allow all of the charge to be transferred into the second electrode's potential well. The sequence is repeated across all electrodes until the charge clouds have been transferred to the serial register.



Figure 3.4: A basic diagram illustrating the order in which the image clocks are switched on to transfer the charge cloud across electrodes.

Once the charge packets have been clocked to the edge of the device, they are then transferred to the readout (serial) register, and are then read out. This register also consists of electrodes, which transfer the charge packets in the orthogonal direction (to the image clocks) towards (an) output node(s) located at the end of the register. The serial clocks $R\phi 1$, $R\phi 2$, and $R\phi 3$ work in the same way as the image clocks (i.e. by switching on and off and overlapping one another sequentially in order to transfer the charge packets across the electrodes).

The charge packets are then transferred through a summing well to the output gate, which is connected to two transistors: the output field effect transistor (FET) and the reset FET. The summing well is an additional pixel capable of collecting charge from a number of pixels, which can be utilised for horizontal binning. (The structure of these components is detailed in Section 3.3.1.1). When the reset FET is switched off (using the reset clock, ϕR), the charge is sampled by the output FET. The change in voltage, ΔV_{FET} , is proportional to the capacitance of the transistor:

$$\Delta V_{FET} = \frac{Q_O}{C_{FET}} G_{FET} \qquad \text{(eq. 3.5),}$$

where C_{FET} is the capacitance of the output FET (typically 0.05-0.1pF), Q_0 is the charge on the output node (in Coulombs), and G_{FET} is the gain of the output transistor. This change in voltage is related to the current between the source gate and drain of the output FET. The charge is then passed through an on-chip amplifier FET. The effect of the on-chip amplifier is governed by a changeable gain factor, which is defined according to the following equation:

$$\frac{V_{out}}{V_{in}} = \frac{gR_{load}}{gR_{load}+1} \qquad (eq. 3.6),$$

where V_{in} is the input voltage measured by the output FET, V_{out} is the amplified voltage, g is the gain of the system, and R_{load} is the resistance of the load resistor. The capacitance and amplifier are specific to the CCD output circuit type (hence the detector will have a specific responsivity/sensitivity characteristic).

Once this process has been performed, the reset transistor is switched back on, the charge in the output node is removed (through applying the drain voltage, V_{RD}), and the output node is reset to a reference voltage level.

The charge, once converted into a voltage and transferred through the on-chip amplifier, is routed to a CDS-ADC chip (Correlated Double Sampling – Analogue to Digital Converter). The CDS-ADC chip performs differencing and amplification of the reset and signal levels and digitisation (for example, 14 bit), detailed in Section 3.2.4 Sources of Noise). The CDS circuit measures a reference voltage after the reset has occurred and a second voltage once the charge has been passed onto the output node. The amplitudes of these two voltages are subtracted and passed through to the ADC for digitisation. The CDS process enables noise associated with the reset level of the pixel to be reduced as well as limiting the bandwidth.

3.2.2.1 Charge Collection and Confinement

A depletion region is formed within the detector when a voltage is applied to the electrodes (that is, an electric field forms in the silicon beneath the electrode). Electrons (generated during the interaction of the incoming signal with the silicon) are swept towards the local minimum in potential within each of the spatially separated pixels. The e-h pairs generated within the depletion region will generally be collected within a small number of neighbouring pixels and therefore exhibit a relatively low level of noise after read out. However, events that arise deeper within the silicon (i.e. in the field-free region, beyond the depletion depth) are likely to diffuse more and therefore spread across a larger number of pixels, resulting in a poorer overall energy resolution. These events typically occur when the energy of the incoming signal is large, resulting in greater penetration depths before absorption. However, when the energy of the incoming signal is relatively low, the photons are more likely to be absorbed before reaching the depletion region, where they can be detected. This results in a reduced quantum efficiency at lower energies. At very high energies, the photon will pass through the device, resulting in a very low likelihood of collecting charge at these energies.

The band-gap of the semiconductor is doped to increase conductivity. In the n-type region there is an excess of electrons whilst in the p-type there is an excess of holes. The depletion region of the semiconductor occurs at the boundary of the n- and p-type regions. The excess of electrons from the n-type region diffuse into the p-type region recombining with the excess holes, and the excess holes are similarly transferred to the n-type region. These migrations cause a larger negative charge in the p-type regions and more positive charge in the n-type regions. Ultimately, the significant charge difference generates a built-in voltage, V_{bi} , and an electric field across the junction. This potential difference forms a region of equilibrium in which the electrons and holes no longer diffuse.

Applying a voltage to the electrode will alter the extent of this: applying a forward bias decreases the size of the depletion region; applying a reverse bias increases the built-in voltage and hence depletion depth.

The electric field is located in the depletion region (beyond the depletion region there is a field free region). The gradient of the electric field is described by Poisson's equation:

$$\frac{d^2 V(x)}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_o} \qquad \text{(eq. 3.7),}$$

where ε_r is the relative dielectric permittivity, ε_0 is the permittivity of free space, and ρ is the charge density (defined as $\rho = qN_A$ for the p-type material, and $\rho = -qN_D$ for the n-type material, where q is the charge of the electron and N_A and N_D are the number of ionised acceptors and donors respectively). Integrating equation 3.7 twice with respect to x and implementing the boundary conditions that the electric field (dV/dx) is zero at x = d (where d is the depletion depth), and that the voltage is the gate voltage, V_g , at x = 0 (at the surface), the following equation can be derived for the voltage across the depletion region:

$$V = \frac{\rho x^2}{\varepsilon_r \varepsilon_o} - \frac{\rho x d}{\varepsilon_r \varepsilon_o} + V_{\rm g} \qquad (\rm eq. \ 3.8).$$

Equation 3.8 can then be used to determine an equation for the depletion depth, d:

$$d = \sqrt{\frac{2\varepsilon_r \varepsilon_o V_g}{\rho}} \qquad (\text{eq. 3.9}).$$

3.2.2.2 Varieties in Structure

As is apparent from equation 3.1, the distance that incoming photons typically travel through the silicon depends on their energy. It is possible that the energy of the photons will be too low to penetrate through the electrode structure and will instead be absorbed before reaching the depletion region. Similarly, the energy of the photon may be so high that it travels through to the other side of the device without being absorbed. There are modifications that can be made to the CCD to optimise the likelihood that certain energies are absorbed and converted into useful signal.

The CCD design described in Section 3.2.1 is known as a front illuminated device: the incoming signal is imaged at the 'front' of the detector, where the electrodes are located, as illustrated in Figure 3.3. However, to enable lower energy X-rays to be detected, it is possible to avoid the electrodes all together (and therefore avoid absorption before reaching the depletion zone), by essentially turning the detector upside down. In these devices, the substrate is thinned and a thin silicon oxide layer forms naturally. Potential wells are still created beneath (above) the electrodes, which are now essentially on the underside of the detector – i.e. the structure in Figure 3.3 is flipped.

Conversely, to enable higher energy X-rays to interact with the silicon within the depletion region, it is possible to extend the depleted layer by either increasing the gate voltage or by using highly doped silicon, as indicated by equation 3.9.

3.2.2.3 Architecture

There are a number of techniques that can be used to minimise image smear (that would otherwise result from signal interacting with the device during readout). The most common approach is to use a full frame device with a shutter, which is utilised in a manner such that all input signal is blocked after the signal integration period. When the use of mechanical mechanisms is not preferred (e.g. for space applications) frame transfer operating modes can be an acceptable alternative. These modes of operation are typically achieved with specifically designed frame storage devices. Alternatively, where electronics complexity is of concern, standard devices can be operated in a 'pseudo frame transfer mode' in which image smear is reduced at the expense of collection efficiency and device imaging area.

Full frame transfer works as described in Section 3.2.1. During integration (i.e. when the signal is converted into charge), all of the pixels in the imaging area are used to collect the signal. Once integration has been completed (defined by the experiment/mission: an optimum integration time in which the signal is not dominated by the number of dark current electrons generated, which increases proportionally with time, and not so long that the full well capacity (total number of electrons collected in each pixel) is surpassed and the image oversaturates), the charge packets are transferred across the full device. If the readout frequency is not fast enough, it is possible that light continues to fall on the detector as the charge packets are transferred across the pixels before reaching the readout register. The effect of this can create smear: the pixels being transferred down the device (to the serial register) may collect more signal even after transfer has begun. Data will therefore be contaminated as it is not necessarily possible to determine whether the signal in the pixel had been acquired during integration or during transfer (these are sometimes known as out of time events).

In frame transfer devices, the imaging area is split into two sections: an image area and a storage area. The charge is collected during integration in the imaging area. Once integration has finished, all of the rows in the imaging area are rapidly transferred into the storage area (using the $I\phi 1$, $I\phi 2$, and $I\phi 3$ clocks). This region is typically shielded (to stop any more light falling on the pixels in that section). Once the charge is in this area, it can be read out of the serial register (at the bottom of the storage unit) at a relatively lower clock frequency using a third set of programmable clocks: the storage clocks ($S\phi 1$, $S\phi 2$, and $S\phi 3$). This setup significantly reduces the chances of smear. However, it requires two sets of imaging electrodes to be controlled at different frequencies, which can consume more power and requires more complex electronics, and can also require an increase in the size and mass of the detector.

Pseudo frame transfer works in the same way as frame transfer except the device will not have been manufactured with two independently controlled regions. Instead, the image and storage regions can be manually applied: an external cover can be used to create the storage region, and the clocks can be sequenced appropriately for different readout frequencies.

3.2.3 Performance Parameters

A CCD detector has a number of performance characteristics that can be modified/enhanced during manufacture in order to tailor performance for specific mission science requirements. These characteristics can be used to optimise the detector's sensitivity and the signal-to-noise ratio (SNR) achievable by the camera

system. The main parameters that can be optimised for this purpose are detailed below, and are used to perform trade-off studies for different science requirements.

3.2.3.1 Dynamic Range

The full-well capacity (FWC) is the maximum number of electrons each potential well (pixel) can store. The FWC depends on the size of the pixel (the size and number of electrodes as well as the depth of the depletion region). A typical value of a CCD FWC for 13µm is 100k electrons (e2v Technologies 2016). The dynamic range (DR) is the ratio of the full well to the read-noise of the system. That is, it describes the capacity of the pixel with relation to the noise in the system. Sources of noise are explicitly described in the Section 3.2.4 Sources of Noise).

One method of analysing the dynamic range of a CCD is to plot a photon transfer curve (PTC), which indicates the response of a CCD at uniformly illuminated light levels. A log-log plot of signal against noise can be used to identify particular regions, dependent on which performance parameter dominates (i.e. the electronics/sampling noise the signal noise, or the structure of the device (Janesick 2001)).



Logscale Mean (ADU)

Figure 3.5: An example photon transfer curve, a log-log curve comparing signal to noise. The first region is dominated by the read noise; once the signal dominates the noise the gradient is then influenced by the shot noise of the signal; at a point in the signal the fixed pattern noise (variance of sensitivity amongst the pixels) dominates the curve until the FWC is achieved.

The first section of the photon transfer curve provided in Figure 3.5 (at the lowest signals) is heavily dominated by the read noise of the camera system. This region
will typically have a gradient of zero as it is the baseline noise taken when the camera is in dark conditions. The second section of the graph begins as soon as the signal begins to dominate over the noise, specifically noise from the signal (shot noise (described in Section 3.2.4.1), which is the statistical variance from the signal). The gradient will typically be ½ as the statistical variance on the number of the electrons generated varies as the square root of the number of incident photons. The third region of the PTC is governed by the fixed pattern noise of the device (the variance of sensitivity and responsivity between each pixel). The fluctuation in the response between pixels (detailed in Section 3.2.3.5) is directly proportional to the signal (Ma et al. 2014),

$$n_{FPN} \propto S \times (PRNU)$$
 (eq. 3.10),

where *S* is the signal and Pixel-Reponse-Non-Uniformity (*PRNU*, see Section 3.2.3.5) is the fixed pattern noise. Finally, the FWC will be reached at a certain signal level, causing charge to spread across neighbouring pixels, which lowers the noise of the system. If any more signal falls onto the device after the FWC has been reached (and before the charge is clocked out), the signal will be integrated in neighbouring pixels, a feature known as blooming. Therefore, the noise of the system is reduced slightly, as the summation of noise in two or more pixels is described as

$$n_{pixTOT} = \sqrt{n_{pix1}^2 + n_{pix2}^2 + \dots + n_{pixm}^2}$$
 (eq. 3.11),

where *n*_{pixm} is the noise is the *m*th pixel and *n*_{pixTOT} is the total noise across *m* pixels.

3.2.3.2 Spectral Response

The probability that an incoming photon will undergo photoionisation when it reaches the silicon structure is a function of the distance travelled by the photon, as detailed in the Section 3.2.1, and described by equation 3.1. It is the thickness of the absorbing material required to attenuate the incoming ray's intensity by a factor of *e*. The quantum efficiency (QE), or spectral response, is the sensitivity of the CCD to the incoming photon at a specific wavelength. It is the percentage of the total number of photons at a specific wavelength that are absorbed and read out as 'useful' signal (the information to be acquired using the CCD). It is dependent on the

absorptivity of the material of each layer of the semiconductor as well as the active thicknesses of the various layers and can be written as:

$$Q = \left(\prod_{m} e^{-\frac{t_{m}}{\mu_{m}}}\right) \left(1 - e^{-\frac{t_{d}}{\mu_{d}}}\right)$$
 (eq. 3.12),

where t_m is the thickness of the mth absorbing layer, t_d is the depth of the depletion layer, and μ_m and μ_d are the linear absorption coefficients of the mth layer and depletion region respectively. The layers of significance for the QE are dependent on which the incoming photon passes through/interacts with. For example, a photon will initially pass through the gate structure made of polysilicon, through an insulating oxide layer (SiO₂) and the silicon nitride layer (Si₃Na₄) to the depletion layer in the epitaxial region.

The QE curve provided in Figure 3.6 is for a standard X-ray CCD with the geometry t_{poly} = 0.835µm, t_{SiO_2} = 0.835µm and $t_{Si_3Na_4}$ = 0.085µm. For comparison, the curves for the depletion regions with depths $t_d = 12\mu m$ and $t_d = 44\mu m$ are included. The linear absorptivity values for the layers were taken from (Henke et al. 1993).



Figure 3.6: The quantum efficiency curve for two depletion depths.

The plots in Figure 3.6 show that a larger depletion depth results in a significantly higher QE (by a factor of 1.5 to 2) between approximately 1.1keV to 1.8keV, and 2.4keV onwards. The curve also highlights the significance of the elemental edges associated with the CCD materials in the device, specifically the oxygen K edge at

0.5keV and silicon K edge at 1.8keV. When the energy of an incoming photon is equal to the binding energy of an electron, there is a significant decrease in the number of generated free electrons. This energy, referred to as the absorption edge, is the minimum edge required to create a hole in the respective electron shell. When the hole is filled by an electron from another shell, specific lines are formed on an X-ray absorption spectrum. These lines are exclusive for each element, depending on their electron binding energies, and so it is possible to determine these drops in absorptivity based on the material of the device.

Optimisations can be made to the detector to improve the QE for specific ranges of energies, as described in Section 3.2.2.2. Deep depleted detectors can be used for higher energies such that photons which would otherwise pass through the substrate will interact with silicon, creating charge that will be collected in the potential wells. Back illuminated CCDs can be used for lower energies, as the lower energy photons will pass straight to the substrate to undergo conversion into charge, rather than potentially being absorbed by the electrodes or oxide layer.

The UV and optical absorption in silicon varies by four orders of magnitude (Janesick 2001). One of the main regions of low QE for a UV and/or optical CCD occurs in the red part of the spectrum: the material becomes more transmissive resulting in a large number of internal reflections contributing to the signal, causing a significant increase in fringing. The fraction of light that is reflected that affects the QE is dependent on the depth of each layer (and their respective refractive indices), the number of layers, and the wavelength of the incoming light (the refractive indices vary with wavelength). To model optical fringing of a CCD, it can be assumed that the intensity absorbed at a given wavelength can be equated to the QE, hence allowing the model to be analysed using geometrical optics. However, the amplitude of the waves must be considered (rather than the intensity, as the intensity does not provide information on the fringing) (Groom et al. 1999).



Figure 3.7: The geometry of the optical light through the layers of a CCD. The light is incident to material at angle θ to the normal, whereas the refracted ray travels at angle θ' to the normal. The reflections, shown by the dashed blue lines, are retarded by phase ϕ and attenuated by factor $e^{-(d/l\cos\theta')}$ across each material.

The geometry for the model is shown in Figure 3.7. The incoming optical light through air is incident to the detector at angle θ . The light partially refracts across the boundary at the first layer and is partially reflected; the fraction of light that is refracted is expressed by *r*. The light that travels through the first layer of thickness *d* is refracted at an angle θ' to the normal. The light at any boundary within the detector (either refracted or reflected) is retarded by phase ϕ , and the amplitude of the light is attenuated by a factor of $\exp(-d/l\cos\theta')$, where *l* is the attenuation length. By determining the fraction of light which is transmitted and reflected at each boundary, and by calculating the extent to which the light is attenuated in each layer, the percentage of the incoming photons which are absorbed by the detector (as useful signal to be read out), i.e. the quantum efficiency, can be approximated using the equation (Groom et al. 1999):

$$QE = 1 - \frac{I_R}{I_0} - \frac{I_T}{I_0} = \frac{(1 - r^2) \left[1 - (1 - r^2) e^{-d/l'} - r^2 e^{-2d/l'} \right]}{1 - 2r^2 e^{-\frac{d}{l'}} \cos \phi + r^4 e^{-2d/l'}} \qquad (\text{eq. 3.13})$$

where I_R/I_0 is the fraction of light which is reflected, I_T/I_0 is the fraction of transmitted light, and *l* is $l \cos \theta'$.

Two example optical QE curves calculated using the equation 3.13 are show in Figure 3.8. In this plot, silicon depths, *d*, of 1500nm and 5000nm, and the light transmitted at an angle of $\theta' = 30^{\circ}$ to the normal have been assumed. It can be seen in the mid optical (~650nm) to NIR region that the fringing plays a significant contribution to the QE, particularly as the depth of silicon increases. One of the main causes is the significant difference between the refractive index of air and that of silicon. Therefore, a method of optimising the optical QE of the detector is to include an AR coating on top of the silicon, which has a refractive index between the two refractive indices.



Figure 3.8: Two optical QE curves, one for a depth of Si of 1.5µm, the other for a depth of 5µm. The effects of fringing on the QE can be seen in the region above 650nm

It is possible to achieve >50% QE for the UV range and to significantly reduce the interference pattern in the optical light with the appropriate choice of thin-film dielectric material, significantly improving the QE of a UV-optical CCD (Hamden et al. 2011), as well as UV optimised silicon. A number of studies have been performed to analyse the optimum material for the AR coating (for example: Lesser 1987; Greer et al. 2013; Hamden et al. 2011); a typical material used for visible wavelengths is Hafnium Oxide (HfO₂). However, it is important to note that if the coating has a

uniform thickness, the reflections and fringing can still occur in various parts of the spectrum. Therefore, to improve the QE, the thickness of the coating should also be varied for optimisation in the specific wavelength range (e.g. for UV, a typical thickness is 10-25nm (Hamden et al. 2011)). The effect has been modelled and an example of the improvement for a solid state detector can be seen in Figure 3.9.

Graded AR coatings can be used for further improvement of the QE. The thickness of the coating can be adjusted across the device such that it is specific to the wavelength being imaged, resulting in a higher QE for the specific wavelengths (as opposed to using one thickness which will be optimal for a significantly smaller wavelength range) (Hamden et al. 2011). An example of a graded coating was used in ESA's MERIS/ENVISAT satellites across the visible wavelength range (Kelt et al. 2006).



Figure 3.9: QE for a CCD with various thicknesses of AR coatings (e2v-Teledyne 2017).

3.2.3.3 Charge Transfer Efficiency

Once the incoming signal has been converted to a charge map, the image has to be transferred to the serial register row by row. There is a very small chance that some charge will be captured by a trap during the transfer process and will no longer remain in the same pixel as the rest of the charge. Furthermore it is possible that charge previously trapped in a pixel is released when other charge packets are being transferred through the pixel. However, as the number of pixels can range from 1024x1024 (e2v Technologies 2017a) to 2048x2048 (e2v Technologies 2016) and above, for optimum CCD performance, it is vital that this effect is reduced as far as possible. It is, therefore, necessary to optimise this procedure to ensure as little information as possible is lost during transfer and readout. This parameter is a measurable characteristic for each device and is known as the charge transfer efficiency (CTE). It is defined as the percentage of charge that has been successfully transferred through all pixels to be read out, and is typically 0.99999 for a modern CCD (Radeka et al. 2009).

A range of factors can affect the CTE of a CCD. If the transfer frequency (the speed of the clocks) is too high, this may result in only a fraction of the charge being attracted to the new potential well before the clock signals are alternated across the electrodes. If the release time of the electrons (detailed below) is too slow compared to the readout speed, some electrons may be kept in previous pixels until the next transfer, causing smear down the image. Another factor is that any defects in the CCD mask or silicon can trap the charge, stopping it from being transferred to the next pixel (this is a particular issue in a high radiation environment, as detailed later in this chapter and in Chapter 4).

The change in the number of trapped electrons, n_{ss} , is calculated by finding the difference in the capture and emission rates from Shockly-Read-Hall theory:

$$\frac{dn_{ss}}{dt} = \sigma v_{th} n_e (N_{ss} - n_{ss}) - \sigma v_{th} n_{ss} N_c \exp\left(\frac{-E}{kT}\right) \quad \text{(eq. 3.15)},$$

where σ is the electron capture process, v_{th} is the thermal speed of the electrons, ne is the density of electrons in the conduction band, N_{ss} is the density of bulk traps at an energy *E* below the conduction band, N_c is the density of states in the conduction band, k is the Stefan-Boltzmann constant, and *T* is the temperature of the device (Shockley & Reed 1952).

The first term in equation 3.15 describes the electron capture rate; it is proportional to the number of states present (in which electrons can be trapped). The second

term describes the electron emission rate; this term is proportional to the available density of states in the conduction band. Integrating equation 3.15 results in equations for the electron capture time constant, τ_c , and the electron emission time constant, τ_e :

$$\tau_c = (\sigma v_{th} n_e)^{-1}$$
 (eq. 3.16)
 $\tau_e = \frac{e^{E/kT}}{\sigma v_{th} N_c}$ (eq. 3.17).

The electron capture in equation 3.16 is not dependent on the number of electrons in the charge packet, whilst the emission time constant in equation 3.17 is dominated by the energy level of the trap. The time scales for these constants are typically of order μ s for the capture time and a few ms for the emission constant, see Chapter 4, Section 4.1.3.

3.2.3.4 Dark Signal Non Uniformity

The dark current (electrons generated from thermal fluctuations in the detector – detailed in Section 3.2.4.2) can vary from pixel to pixel in a CCD, an effect referred to as Dark Signal Non Uniformity (DSNU). This value is defined as the RMS deviation of the pixel signal with no ambient light present. The DSNU contributes to the noise of the overall system on a pixel to pixel basis (Nakamura 2006). Therefore, a dark signal map that corrects for non-uniformities at the pixel level can be applied to mitigate this issue. An example DSNU image (Hytti 2005) is provided in Figure 3.10.



Figure 3.10: An example image representing a detector with high DSNU (Hytti 2005)

3.2.3.5 Pixel Response Non Uniformity

The pixel response non uniformity (PRNU), also known as fixed pattern noise, is a measure of the inhomogeneity in response between pixels. PRNU reveals the deviation of the pixel response relative to the mean pixel response. Deviation in pixel response may be a result of inhomogeneities formed during the manufacture of the CCD, resulting in some pixels exhibiting a different responsivity to the incoming light than other pixels. An example PRNU map is provided in Figure 3.11.



Figure 3.11: an example PRNU map.

3.2.3.6 Linearity

Linearity is a measure of the system gain as a function of signal size. An ideal camera exhibits a constant gain across all signal levels. This characteristic is particularly important when comparing different signal levels. In general, the signal should vary linearly with the exposure time. However, in reality this may not be the case. The signal's variance with exposure time is described using the equation

 $S = kt^{\gamma}$ (eq. 3.18),

where *S* is the signal, *k* is a constant of linear proportionality, *t* is the exposure time, and γ is the measure of linearity. Ideally, γ should be equal to 1.

3.2.4 Sources of Noise

The noise in the system can significantly degrade the achievable SNR of the detector. In the following sections, the most common and effective contributors to the overall noise are described.

3.2.4.1 Signal Shot Noise

During photoionisation there is a statistical variation in the number of electron-hole pairs promoted into the conduction band, which results in a significant noise component for high level signals. However, it is important to note that this variation depends on the wavelength of the incoming photon. As described in Section 3.2.1 Charge Generation, an optical photon generates one electron-hole pair for each photon interaction with the silicon. The statistical variation on this interaction is described according to Poissonian statistics. If the mean signal has *n* electrons per pixel during readout, the statistical variation is described as

$$\sigma_{shot,opt} = \sqrt{n}$$
 (eq. 3.19).

However, in the case of a higher energy incident photon, such as an X-ray, there is an energy required to excite the electrons into e-h pairs and causing the cascade/Auger process. This energy, ω , for silicon is 3.62eV (and is weakly temperature dependent). The mean number of electrons generated by a high energy photon of energy, *E*, is described as

$$n = \frac{E}{\omega} \qquad (\text{eq. 3.20}).$$

However, during each photoionisation process some energy is imparted to the surrounding silicon lattice. Fano (1947) found that this process reduces the expected variance on the number of e-h generated during the photoionisation process. This limit on the energy of the transitions is described by a factor, known as the Fano factor, *f*, such that the statistical variance is described by

$$\sigma_{shot,fano} = \sqrt{fn} = \sqrt{\frac{fE}{\omega}}$$
 (eq. 3.21),

where f = 0.11 for silicon. For example, using equation 3.21, the shot noise from a magnesium K α X-ray (1.3keV) is 6 electrons, whereas for a zinc K α X-ray (8.6keV), the shot noise is 16 electrons.

3.2.4.2 Dark Current

Dark signal is generated as electrons are promoted into the conduction band via random thermal energy fluctuations in the detector (as opposed to via the absorption of incoming photons). As these free dark electrons are formed in the same way and at the same time as those representing the signal, it is not possible to differentiate between them within a charge packet/pixel.

As the dark current electrons are generated by thermal energy in the CCD, the number of electrons varies with the operating temperature of the device, (this relationship depends on the structure and form of the device). Furthermore, the average total dark current signal increases proportionally over time. Therefore, operating the device at a lower temperature and performing readout and integration over shorter periods of time reduces the number of dark current electrons generated. An example of a detector dark current curve across the temperature range 252K and 295K is shown in Figure 3.12. This curve is representative of a back-illuminated AIMO CCD42-10 from Teledyne-e2v Technologies (e2v Technologies 2016). The curves in Figure 3.13 illustrate the difference in dark current between an AIMO and NIMO device, specifically the back-illuminated CCD47-20 from Teledyne-e2v Technologies (e2v Technologies 2017a).



Figure 3.12: A plot representing the dark current for a CCD42-10 across the temperature range 252K to 295K



Figure 3.13: A plot comparing the dark current of a NIMO and AIMO CCD47-20 device across the temperature range of 252K to 295K.

The dark current noise is expressed as

$$\sigma_D = \sqrt{I_D t} \qquad \text{(eq. 3.22),}$$

where I_D is the dark current per second and t is the integration time. Dark current electrons may be generated in: the states on the surface (in the Si and SiO₂ layers), the depletion region of the detector, and the field free region – electrons generated in the latter two are usually referred to as bulk dark current (Widenhorn et al. 2002).

The main process of reducing bulk dark current (caused from impurities in the depletion and field free regions) is by cooling the device. However, the surface dark current contributes to the dark current noise more than the bulk dark current (Janesick 2001).

An important aspect of dark current signal levels is the thermal stability with time while the detector is operating. The number of dark current electrons generated per second changes for different temperatures. It is possible during a mission that the temperature the detector is operated at may vary (from ± 0.25 K due to systematic error on the temperature control). Therefore, to predict/model the noise performance of a detector during the mission lifetime, the variance of the dark current generation across a temperature must be understood. An example of the change in dark current generation across the 252K to 295K temperature range for back-illuminated AIMO CCD42-10 is shown in Figure 3.14. The curve shows that a dark current generation varies by $\pm 0.03e/pix/s$ at 260K, whereas the variance at 288K is $\pm 1e/pix/s$.



Figure 3.14: A plot showing the variance in dark current generation for a back-illuminated AIMO CCD42-10 across 252K and 295K.

3.2.4.3 Reset Noise

Once the charge cloud has been measured, the output node must be reset to a 'starting' voltage, V_{rd} (reset drain voltage), ready to read the next charge packet. There is a noise associated with this reset process, affected by both Johnson and thermal noise due to the FET channel resistance. For a given temperature, the reset noise is defined by

$$n_{reset} = \sqrt{\frac{kT}{C_0}} \qquad (eq. 3.23),$$

where k is the Stefan-Boltzmann constant, T is the temperature of the device, and C_0 is the capacitance of the output node.

Utilising the CDS process significantly reduces the noise associated with variations in the reset level. The fluctuations in the reset level between each pixel are effectively removed by sampling the voltage level before and after measuring the signal in each pixel, the difference between the two is determined using an operational amplifier, and the resulting corrected level is digitised and stored.

3.2.4.4 ADC Quantisation

There are electrons produced which are associated with the noise in the digitisation of the corrected level calculated during the CDS process. The uncertainty in the value is known as the ADC quantisation error and is defined as the RMS of the ADC transfer function. The analogue signal is converted into a digital number represented by a sequence of bits. The maximum error of an ideal ADC is $\pm \frac{1}{2}$ LSB (least significant bit) (Kester 2008). It is also possible to represent the error as $\pm \frac{1}{2}q$, where q is the peak-to-peak amplitude of the LSB, visible in Figure 3.15. To calculate the error when the analogue value is represented by a range of bits, it is possible to represent the error as a sawtooth waveform (Kester 2008), illustrated in Figure 3.15.



Figure 3.15: The quantisation noise as a function of time in a sawtooth waveform, with a peak-to-peak amplitude of *q* (Kester, 2008).

Calculating the RMS of a uniform sawtooth waveform with the range from -q/2 to +q/2, the following equation is derived:

$$RMS_{qn} = \sqrt{\frac{1}{q} \int_{-\frac{q}{2}}^{\frac{q}{2}} x^2 dx} = \frac{q}{12}$$
 (eq. 3.24)

Therefore, the quantisation noise can be described as $1/\sqrt{12}$. To convert this noise into electrons, the gain of the system (the number of electrons per digitised value) must be accounted for, and is given by

$$gain = \frac{S_{max}}{2^{n}-1}$$
 (eq. 3.25),

where S_{max} is the maximum signal that can be acquired by the CCD (given in electrons), and *n* is the number of digitisation bits produced by the ADC (the bits assigned to the measured charge).

3.2.4.5 Transistor/FET Noise

Electrons are generated in the output transistor, which can add to the noise of the system, a contributor known as flicker noise. The electrons generated from flicker noise are thought to arise from mobility fluctuations in the channel of the FET, or trapping and emission of electrons in the channel or at the silicon oxide surface near the FET (Janesick 2001). The noise dominates at low frequencies (<100Hz) with a noise spectral density of $\frac{1}{f}$ (see Figure 3.16). It is possible to reduce flicker noise by increasing the speed at which the electrons move through the FET (McHugh 2018).

The electrons will have a lower probability of becoming trapped and emitted (defined in equations 3.16 and 3.17). The flicker noise has a flat autocorrelation function (Schmid 2008) and therefore it is possible to reduce the noise through the CDS process by subtracting the two correlated samples (Kawahito et al. 2009; Schmid 2008).

Another noise component from the output transistor is Johnson noise. Electrons generated through Johnson noise arise for thermal fluctuations and is referred to as white noise in the FET. This thermal noise has a flat frequency distribution.

The flicker noise varies with the readout frequency, *f*, by the relation

$$\sigma_{flicker} = \sqrt{1 + \frac{f_c}{f}} \qquad (eq. 3.26),$$

where f_c is the corner frequency: the frequency at which the flicker noise does not dominate the white noise (see Figure 3.16).



Figure 3.16: MOSFET noise in a camera system for a range of readout frequencies, showing how the flicker noise dominates at lower bandwidths (McHugh, 2018).

3.2.4.6 Read Noise

The overall combination of the noise sources arising from the CCD and its associated electronics is often referred to as the read noise, σ_R . This noise is the quadrature sum of the standard deviations of the various noise components described above:

$$\sigma_R = \sqrt{\sigma_{reset}^2 + \sigma_{ADC}^2 + \sigma_{FET}^2 + \cdots} \quad (eq. 3.27).$$

The three sources of noise discussed above are arguably the most significant/primary sources of noise, such that the full width half maximum (FWHM) an X-ray energy, *E*, peak is:

$$FWHM(eV) = 2.355 \times 3.65 \sqrt{\sigma_R^2 + I_D t + \frac{fE}{\omega}}$$
 (eq. 3.28)

where ω is the energy required to produce an e-h pair (for silicon, $\omega \approx 3.67$ eV at room temperature). Equation 3.28 can be used for most systems to calculate the SNR of a system for various temperatures and photon rates, across a specific timescale. For example, assuming an Iron K α X-ray (6.4keV) is incident on an AIMO CCD, with a dark current, *I*_D, is 50 electrons e/pix/s. If the read noise of the system is 10 electrons, the CCD integrates the signal at 1s and is operated at room temperature, the FWHM of the energy peak is 156eV. If the CCD was integrated for 10s, the FWHM would only increase to 240eV. In comparison, if the same system was used with a NIMO CCD, with a dark current of 20,000e/pix/s, the FWHM of the same energy peak integrated for 1s would be 1224eV. Analysis using equation 3.28 allows for identification of the performance requirements of a detector in a particular mission scenario: for example, to differentiate between the Iron K α and K $_{\beta}$ (7.1keV) energy peaks, either an AIMO detector must be used, or a NIMO device operated at a much lower temperature and integrated for ~0.1s.

Equation 3.28 can be modified to calculate the FWHM of an energy peak for a photon with a lower energy (that is, a photon which will excite one electron in the silicon, rather than a cascade). The fano factor does not apply (described in Section 3.2.4.1), only the photon shot noise (equation 3.19) and hence the equation becomes

$$FWHM(eV) = 2.355 \times 3.65 \sqrt{\sigma_R^2 + I_D t + n}$$
 (eq. 3.29)

For 80,000 532nm photons incident on an AIMO CCD, with a dark current, *I*_D, is 50 electrons e/pix/s, the read noise of the system is 10 electrons, the CCD integrates

the signal at 1s and is operated at room temperature, the FWHM of the energy peak is 2,434eV.

3.2.4.7 Pre-Amplifier Noise

The signal acquired from the CCD may require amplification, performed by an external amplifier, which also has an associated noise. This noise is defined as

$$\sigma_{pre-amp} = \frac{1.7nV}{\sqrt{F}} \qquad (eq. 3.30),$$

where F is the bandwidth frequency of the system. The input voltage noise 1.7nV is specific to the AD829 op-amp (Analogue Devices Inc. 1998) and will vary based on the type of op-amp used in the pre-amplifier circuit.

3.2.4.8 Ambient Light

Although the vast majority of sources of noise occur in the CCD and/or its associated electronics, it is still important to consider external contributions. Ambient light is any light/signal that falls on the CCD which is not considered to be 'useful' information. This can originate from a number of different sources, including sunlight and nearby pieces of equipment that emit their own light. Charge generated from ambient light is indistinguishable from the electrons generated by the useful signal (although in some applications, the spatial distribution of the useful signal may make it possible to accurately determine the ambient light level). Ambient light will fill the potential well with unwanted electrons, i.e. decreasing the available capacity for collecting signal within each pixel, and reducing the SNR.

It is important when constructing the instrument to consider ways of reducing ambient light. Typical methods include baffling the detector with an optical enclosure such that it can only image the useful input signal, or only performing scientific acquisitions in dark conditions. In spectroscopy, it is possible to determine the ambient light levels from off order pixels: analysing the mean intensity in a region of interest separate from the order(s) and subtracting the value from the diffracted signal will remove the ambient light offset applied to the orders.

3.3 COMPLEMENTARY METAL-OXIDE-SEMICONDUCTOR (CMOS)

3.3.1 Charge Generation and Structure

Although conceived before the CCD (Janesick 2004), the complementary metaloxide-semiconductor (CMOS) – often referred to as active pixel sensors (APS) – were first suggested in the late 1960's (Dyck & Weckler 1968; Weckler 1967). For the first couple of decades, MOS devices were periodically researched whilst most applications utilised CCDs. However, by the early 1990s CMOS detectors were becoming more popular. The optimisation in circuitry, fundamentally small pixel sizes, lower cost manufacturing processes, and lower power consumption (compared to a CCD), has led to CMOS detectors being used in a large number of industries and applications (Mendis et al. 1997).

The primary difference between a CMOS detector and a CCD is that each MOS pixel in a CMOS device (made of monolithic silicon), contains its own imaging region and dedicated read out circuitry consisting of three transistors (one for transferring the charge to the ADC, one for row/column selection, and one for reset). The circuitry typically incorporated in each pixel is shown in Figure 3.17. The imaging region consists of a photodiode with a grounded anode and floating cathode. The photodiode is reversed biased, and thus forms a depletion region in which charge is collected, as described in Section 3.2.1 Charge Generation. However, unlike for the CCD, the electron cloud in each depletion region/pixel for a CMOS device does not need to be transferred across neighbouring pixels in order to be read out. Instead, the dedicated circuitry allows the signal to be amplified through a source-follower and read out directly (see Sections 3.3.1.1 and 3.3.1.2). One column (or row) of CMOS pixels is operated by a readout circuit, allowing selective readout of regions of interest on the detector. This structure can be utilised to provide a faster readout speed if only a small section of pixels needs to be read out. The amplified charge cloud is then sampled by circuitry.



Figure 3.17: Schematic of the three transistor circuitry used in each CMOS pixel. Two voltages are shown here: the supply voltage, V_{DD} , and the reset voltage, V_{RD} . The signal is collected in the photodiode and passed through the source follower (amplifier transistor and load transistor). It is sampled through the column bus.

3.3.1.1 MOSFET

The Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET) is used in both CCDs and CMOS detectors (as either a switch or an amplifier). In the CCD, it is used as the read out circuitry once the charge clouds have been clocked out of the serial register. In the CMOS APS, each pixel has a number of its own MOSFET circuits for readout, amplification, and noise reduction. Figure 3.18 illustrates the cross-section of a MOSFET and its related circuitry.



Figure 3.18: A cross-section of a MOSFET, showing the electrodes (source, V_{S} ; gate, V_G ; and drain, V_D) on top of the semiconductor n- and p-type silicon – note that the gate electrode is located on the insulating silicon oxide layer. The region in between the n-type silicon (length *L*) is where the depletion zone is formed when a reverse bias is applied to the gate electrode. (V_B is the substrate voltage).

The MOSFET consists of a p-type silicon substrate and two implanted n-type silicon regions: the source (on the left of Figure 3.18) and the drain (the right region of Figure 3.18). The flow of the electrons is from the source region to the drain region, controlled by the source and drain electrodes located on top of the substrate, with respective voltages V_S and V_D . A gate electrode is located on top of the insulating silicon oxide in between the source and drain terminals, with voltage V_G (there is also a substrate/body voltage, V_B , but this is usually set to 0V). When V_G is set to 0, the MOSFET is known as an enhancement MOSFET and there is a depletion region formed below the electrodes. That is, there is no flow of electrons from the source to the drain (unless a positive bias is applied); in this mode an enhancement MOSFET is typically used as a switch. When a bias is applied to V_G , a depletion zone is formed beneath the electrode, between the two n-type regions, with length *L*. The MOSFET in this case is referred to as the depletion MOSFET, in which conduction between the source and drain regions is enabled. The flow of current from the drain to the source is described using the equation

$$I_{DS} = \frac{1}{2} \mu C_0 \frac{W}{L} (V_G - V_T)^2 \qquad \text{(eq. 3.31)},$$

where *L* is the effective channel length between the source and drain, *W* is the channel width, *C*₀ is the effective gate capacitance per unit area, and μ is the carrier mobility. Equation 3.31 shows that if the gate voltage (*V*_G) is below the threshold voltage, *V*_T, there will be no flow of electrons between the source and drain regions.

3.3.1.2 Source Follower

Each CMOS pixel consists of a source follower circuit, comprising two MOSFETs connected in series: the "follower" and "load" transistors. A schematic of the source follower circuit is shown in Figure 3.19. The source follower is used to buffer the photodiode voltage to the output of the sensor.



Figure 3.19: The source follower circuit.

The load MOSFET supplies a constant current across the two transistors, governed by the load voltage, V_{LG} . The supply voltage, *VDD*, determines the gate voltage according to the equation:

$$V_G = V_{in} - V_{out}$$
 (eq. 3.32),

where *V*_{in} and *V*_{out} are the input and output voltages of the circuit, respectively. This gate voltage is adjusted such that is equates to the current flowing through it.

3.3.2 Pixel Operation and Structure Variations

By applying a bias across the gate electrode of the reset MOSFET, the photodiode in the CMOS pixel is initially set to a calculated reset level and remains in a floating state (El-Desouki et al. 2009). The gate voltage is set to 0 to form the depletion region (described in Section 3.3.1.1) and the signal is converted into charge, as described in Section 3.2.1. The second transistor, the row selector is then switched on in the same manner. At this point, the amplifier transistor (the follower transistor in Figure 3.19) is also biased through its gate electrode, as is the load transistor (positioned after the output bus in Figure 3.17), which fully connects/completes the source follower circuit. *V*_{out} is then sampled by the output terminal of the pixel. The reset clock, ϕR , then applies the reset bias, discharging the photodiode, and resetting it such that it can collect more signal from the base level once the previous signal has been read out.

3.3.2.1 3T

The most common pixel design in a CMOS detector is the 3-transistor (3T) pixel and utilises the functionality described in Section 3.3.2 Pixel Operation and Structure Variations. The main structure of the 3T pixel is a source follower (with the amplifier transistor as the follower), and the row/column select and row/column load transistors (governing all pixels in one row/column).

3.3.2.2 4T

The difference between a 3T and 4T pixel design is that the 4T pixel includes a transfer gate between the photodiode and sense node. In the 4T architecture, the charge collection and readout node are separated, unlike in the 3T architecture (Vu et al. 2008). The purpose of this transistor is to improve the transfer efficiency of the charge from the photodiode and sense node by utilising the CDS process: during integration, the transistor is switched off and the charge is collected in the photodiode. At the end of integration, the transistor is switched on and the charge is passed through a floating diffusion node. A voltage is then applied through the

diffusion, resulting in the photodiode becoming fully depleted, allowing for a reduction in noise in the transfer of the charge.

The transistor is sampled before and after being switched on and the CDS process is performed. A key advantage of the 4T architecture is that through the CDS process, the kTC (or reset) noise is reduced (Coath et al. 2009). Another advantage over the 3T design is the ability to obtain a higher conversion gain. In the 3T architecture, the capacitance is determined by the diode. In the 4T architecture it is the diffusion node that determines the capacitance, which can be designed to provide a smaller capacitance (if necessary for the application of the CMOS device) (Coath et al. 2009). Integrating a smaller capacitance from the diffusion node can allow for a greater sensitivity of charge.

3.3.2.3 5T

In Sections 3.3.2.1 and 3.3.2.2 the CMOS pixels described follow the same reset process: when integration has completed, the row (or column) circuitry must move from pixel to pixel to readout the charge. When the first pixel has been read out it will then begin integration again, whilst the rest of the pixels along the row are read out. The integration start times of each pixel are offset by the read time, a process which can cause smear/blur in the final image, especially if the object is moving during acquisition. In the 5T design, the fifth transistor is a global reset. Its purpose it to reset all pixels at the same time such that they all integrate simultaneously (Janesick 2004).

3.3.3 CMOS Specific Parameters

CMOS devices share a number of similar performance characteristics (and sources of noise) with CCDs, all of which are described in Sections 3.2.3 Performance Parameters and 3.2.4 Sources of Noise. However, due to the significant difference between the architecture of the two detector types (i.e. that each pixel in a CMOS device has its own circuitry) additional parameters are described here which are specifically associated with CMOS devices: fill factor and fixed pattern noise.

3.3.3.1 Fill Factor

Due to the pixels in a CMOS device incorporating their own read-out circuitry, the active area of each pixel may be reduced by the presence of the transistors, hence a smaller portion of each pixel is photosensitive. A characteristic often referred to in a APS device is the fill factor, *FF*, defined as:

$$FF = \frac{A_{ph}}{A_{pix}}\%$$
 (eq. 3.33).

That is, it is the ratio of the photosensitive area, *A_{ph}*, to the total pixel area, *A_{pix}*. The fill factor is related to the quantum efficiency of the device, through the equation

$$\eta_{int} = \frac{\eta}{FF} \%$$
 (eq. 3.34),

where η_{int} is the interacting QE (the fraction of incoming photons that are turned into useful signal) and η is the measured QE.

Typically, a front illuminated CMOS device has approximately 19% of the pixel area sensitive to light. Within that fraction, the fill factor has been calculated on average to be \sim 30% (Waltham 2013). This value is particularly low due to reflection from the bus part of the circuitry, as well as charge formed in the field free region and being 'lost' in the transistor electronics (Waltham 2013). It is possible to increase the fill factor of an APS, and hence the QE of the detector, by fabricating a sheet of microlenses placed on top of the device. The microlenses focus the incoming signal specifically onto the photosensitive regions of the pixels.

3.3.3.2 FPN

Sources of noise in a CMOS APS detector include: flicker/FET noise, reset noise, shot noise, and dark current. Due to the pixels having their own circuitry and being manufactured independently to one another, there is also a significant increase in the variation in photo-response from pixel to pixel. This is commonly referred to as Fixed Pattern Noise (FPN), which is the measure of the variability of the signal spatially from pixel to pixel. The contributors of FPN are usually generated during the fabrication process: for example, source followers may have variations of the DC offset and/or gain values. Furthermore, the variability across pixels can increase the PRNU values, as well as the DSNU. Moreover, radiation effects can introduced FPN if the shielding over the device is not uniform (Janesick 2004).

The responsivity of the CMOS detector may also be affected by the pixel response variability between the pixels. The responsivity of a pixel varies with the photodiode capacitance.

3.4 RADIATION DAMAGE IN DETECTORS

The radiation environment in space is complex and unstable, with a high number of sources of varying radiation. The Sun's solar wind carries very high energetic particles across the Solar System, with solar flares ejecting protons in specific directions and at random times (Schrijver & Beer 2014). Planetary systems, such as the Jovian system, have also been found to have complex radiation environments affecting all bodies and satellites within the planet's vicinity (Garrett et al. 2012). The planet's magnetic field can emit cyclotron radiation (Vanhamäki 2011), caused by the radiation belt regions surrounding the planets. The sources of radiation are not restricted to the Solar System – galactic cosmic rays in the form of high energy particles (such as protons or alpha particles) add to the complex environment. However, no matter the source of the radiation, it is vital to determine how the environment affects a mission's analytical instruments and hence ability to meet their science requirements. In order to ensure that the science objectives will be met throughout the duration of the mission, it is important to fully model the radiation environment and test the effects of the individual components of the instrument during the mission proposal and design phase to determine the optimum instrument and spacecraft design.

There are various sources of shielding used for the spacecraft and instruments: the planet's magnetic field (that can trap the solar wind and cosmic rays; and physical shielding protecting the spacecraft and instruments). The former is not uniform nor predictable and may not be relevant to smaller bodies, such as moons. Therefore, it is important to design the instrument with inherent protection during the mission lifetime.

A typical material used for shielding is Aluminium or a high atomic number metal (e.g. Tantalum). Aluminium shielding with a thickness of ~5mm can protect the instrument from up to 5MeV electrons. Example curves of the displacement and ionising damage as a function of Aluminium shielding depth on a Europa lander (20 day mission) are shown in Figure 3.20.

However, other forms of radiation (for example higher energy or heavier particles; or cosmic rays) can be more challenging to shield and, therefore, can degrade the performance of instrument components. Furthermore, it may be necessary for the detector to be unshielded in order to acquire the necessary scientific data, and hence will be subject to the full radiation environment (e.g. the open focal plane of an X-ray or optical telescope (see, for example: O'Dell et al. 2000; Terrazas et al. 2017)). When a high energy, charged particle is incident on a detector, nearly all of its energy (99.9%) is absorbed. As explained in Section 3.2.1, this absorption causes e-h pairs to form in the detector. The generation of the charge clouds due to these high energy particles is called Ionising Energy Loss (IEL) and results in ionising radiation damage. Lower energy radiation affects the detector via nonionizing interactions, for instance displacing the silicon atoms in the silicon lattice. This form of interaction is known as Non-Ionising Energy Loss (NIEL) and causes displacement (bulk) damage in the detector. IEL and NIEL are detailed in the following sections, including their effects on the detectors.



Figure 3.20: Graphs of the ionising damage (top) and displacement damage (bottom) as a function of the aluminium shield on a Europa lander 20 day mission. (RDF = radiation design factor, the ratio of the component radiation tolerance against the radiation environment). (Kokorowski, 2018)

3.4.1 Ionising Radiation Damage

Ionising radiation can cause damage to the oxide layer in a MOS silicon detector. High energy particles can cause ionisation in the SiO₂ layer (similar to the photoelectric effect), generating e-h pairs. Typically, this damage is caused by energetic photons and electrons (heavier particles tend to cause displacement damage).

The holes generated tend to become trapped in the oxide layer, altering the level of number of electrons in the charge packets. This increase in positive particles generates a flatband voltage (typically 0.1V per 10³ rad in silicon), affecting the surface and gate voltages, shifting the biases applied to the system (clocks, amplifier, output node).

A second effect occurs in the Si-SiO₂ interface, where the high energy particles break the lattice bonds resulting in the formation of interface states. The newly formed states can also create a shift in the flatband voltage, having the same effect as described above, but also can significantly increase the number of dark current electrons generated. This damage may arise from relatively low radiation levels, where radiation as low as 5krad can increase the number of dark current electrons by two orders of magnitude (Janesick 2001).

The following performance characteristics of the detector are affected by ionising radiation damage:

- **Dark current.** The dark current generation level significantly increases due to the traps created at the silicon-silicon dioxide interface. In turn, the SNR of the camera system will decrease.
- **DSNU.** The radiation damage is not uniform across the surface of the detector as it is dependent on where the interactions of the high energy particles occur. Therefore, there will be a non-uniformity in the increase of dark current electrons generated from pixel to pixel.
- **PRNU.** Similar to DSNU, the non-uniform distributed traps created in the silicon capture electrons from the charge clouds randomly from pixel to pixel. Therefore, if the pixels integrated the same amount of charge (for example with a flat field illumination) the fluctuation of charge across the pixels will

increase compared to a non-radiation damaged device, hence increasing the PRNU.

- **FWC.** The ionising radiation affects the FWC in two ways. First, as the dark current generation increases, there is less space for signal to be stored in the pixels. Second, the positive bias created affects the operating voltages thereby altering the size of the potential wells in the underlying silicon. This, in turn, decreases the size of the full-well capacity (100-200mV per krad).
- **QE/responsivity.** The generation of the flatband voltage can decrease the size of the potential wells created, used for collecting the charge converted from the incoming photons. Therefore, there will be a reduction in the number of electrons collected in each pixel; that is, with the decrease in potential well size, electrons generated in the silicon from higher energy photons may not experience the force from the electric field and hence may not be collected in the pixels. Therefore, the QE will be altered/degraded as the number of useful signal acquired will be lower than before the generation of the flatband voltage.

Ionising radiation damage is typically referred to in terms of the total dose received by the detector, which is defined as:

$$D = \frac{dE}{dM} \qquad (\text{eq. 3.35}),$$

where *dE* is the average energy absorbed by the detector of mass *dM*. The unit of the total dose is radiation absorbed dose (rad), which is equivalent to 100 ergs (10^{-7} J) of energy imparted on 1g of material (or 0.01J/kg). Specifically in silicon, the absorbed dose (defined as the energy absorbed per unit mass of silicon) is given in units of gray (Gy), where 1Gy = 100rad = 1J/kg. The total dose in the epitaxial region of a silicon CCD, assuming uniform incident radiation, is given by:

$$D = \frac{S(e) \times 3.65(eV/electron) \times 1.6 \times 10^{-14}}{\rho_{Si} x_{width} x_{height} x_{depth}} \qquad (eq. 3.36),$$

where S(e) is the average charge generated in each pixel measured in electrons, ρ_{si} is the density of silicon (2.3g/cm³), and x_{width} , x_{height} , x_{depth} are the width, height, and depth of the pixel.

3.4.1.1 Prevention of IEL

It possible for the detector to 'recover' from the traps created after a few days, through the process of annealing (when trapped holes detrap). One type of annealing, known as tunnel annealing, can occur due to electrons in the silicon tunnelling through to the oxide layer, which can recombine with the trapped holes. A second type, thermal annealing, occurs when thermal energy causes the holes to escape the trap. Annealing can occur over a few days, depending on the distance of the trap from the silicon-silicon oxide interface and the temperature of the device (Huang et al. 2009; Kyle et al. 2008). Annealing can be manually applied to a detector by cycling the detector to a warmer temperature, allowing the holes to escape at a faster rate.

Other ways to minimise the effects of ionising radiation damage are to select an appropriate device architecture (i.e. an AIMO CCD which exhibits a significantly lower level of dark current).

The ionisation damage is more significant when biases are applied to the electrodes on the CCD (as they are altered by the generation of the flatband voltage (Ergin et al. 2010; D. Burt et al. 2017), described in more detail in Section 3.4.1 Ionising Radiation Damage). Therefore, a non-powered CCD will suffer less ionising damage. However, powering the CCD and applying the biases will attract the electrons into the potential wells and the holes to the gate electrode, hence reducing the number of holes trapped at the interface. A similar trade-off should be performed when analysing the optimum temperature to operate the detector. If the detector is operated at a cold temperature (e.g. ~173K) the number of dark current electrons generated will be significantly lower. Furthermore, lower temperatures slow the diffusion of e-h pairs, encouraging the recombination process (Janesick 2001). However, the thermal annealing process will occur at a much slower rate at such cold temperatures.

3.4.2 Displacement/Bulk Damage

Displacement (bulk) damage occurs across a broader range of detectors (as opposed to IEL which only occurs in detectors that incorporate an oxide layer), and

affects the epitaxial layer. It occurs when heavy particles (protons/neutrons) collide with silicon atoms and displace their position within the lattice, causing vacancies and interstitial pairs to form, so called Frenkel pairs (see Figure 3.21). This interaction occurs when the incoming particle travels past the nuclei of the silicon atom. It is possible that this elastic collision imparts enough energy to cause the initial displaced atom to disturb more atoms. Most of these vacancy pairs recombine (~98%, depending on temperature; at room temperature recombination occurs over a few seconds to a minute, others can occur over up to a year (Janesick 2001)). Those that do not recombine end up in interstitial positions in the bulk silicon, forming stable new energy levels (known as traps). It is possible for a dose of 25rad protons to cause displacement damage.



Figure 3.21: Diagram illustrating displacement damage: an incoming proton (left image) knocks the Si-atom in the lattice, which forms holes/vacancies REF interstitial pairs of atoms throughout the lattice (right image).

In comparison to proton displacement damage, neutrons cause a similar but significantly different effect. Due to the neutron having a smaller cross section (probability that the particle will interact with the silicon, described in more detail later in this section and in equation 3.39), the neutron will interact with fewer silicon atoms. However, the proton interaction is coulombic but the neutron interaction is nuclear, causing it to impart more energy in the initial interaction resulting in the displaced atom colliding with a larger number of secondary atoms. Therefore, the main difference between the two interactions is that more annealing will take place after neutron damage (due to a larger portion of the lattice being displaced) and a larger number of traps will form in the pixel.

Traps can hold charge for 'random' periods of time that diffuse during device operation. As, statistically, the charge may be released at any point (potentially after the charge packet has been transferred to the neighbouring pixel), it is possible that the trapped charge is released when signal from a different charge packet passes through the pixel, sometime later. Due to the radiation induced creation of the traps, the following detector parameters are affected by displacement damage:

- **Dark current:** Due to the generation of traps in the potential well, it is likely that a larger number of dark current electrons will be excited from the thermal fluctuations in the detector. The dark current generation increases linearly with radiation dose (Hopkinson 2000), described in more detail and modelled in Chapter 4.
- **Dark Spikes:** The increase in the number of dark current electrons generated due to NIEL effects, and captured in the non-uniformly distributed traps, results in a relatively intense level of dark current in random pixels. This increase is known as a dark spike. It is possible to estimate the density of dark spikes generated in the silicon for a given proton energy, given by equations 3.40 and 3.41, described at the end of this section.
- **CTE:** There is a possibility that charge will be caught by a trap formed by the radiation in the potential well / channel regions. The probability of this occurring will increase as a larger number of traps is generated. Therefore, the higher the number of traps, the more likely it is that the charge clouds may not be completely transferred from pixel to pixel, as some of the electrons from charge cloud may be held back in the traps. Therefore, the charge transfer efficiency will be degraded. This degradation is described in more detail in Chapter 4.

The voltage within the detector may also be affected by NIEL. The defects caused by the displacements can result in electrons tunnelling through a potential barrier from the valance band to the conduction band, hence changing the net charge in the device.

For displacement damage, incoming radiation is measured in terms of fluence. Fluence and total dose are related by

$$D = kFS \qquad (eq. 3.37),$$

where *k* is a constant (1.602x10⁻⁵ergs/MeV), *F* is the fluence (with units particles/cm²), and *S* is the stopping power of the particle (MeVcm²mg⁻¹), defined by the energy exchange, dE, (MeVcm³mg⁻¹) in a mass of depth dx (cm),

$$S = \frac{dE}{dx} \qquad (\text{eq. 3.38}).$$

Equation 3.38 shows that the greater the stopping power, the greater the energy loss and hence total dose received by the detector.

There is a probability that the particle will interact with the silicon atom, which is described by the cross section. It is the area of the silicon that is available to interact with the incoming particle. A larger cross section means that the available area for interaction is greater than the size of the incoming particle. In terms of radiation interaction, the cross section is defined by the fraction of alpha particles that recoil from a target, divided by the target's nuclei density and target thickness. It is related to the mean free path of the incoming particle, λ (cm), which describes the average distance the incoming particle will travel before it interacts with the target silicon, defined as

$$\lambda = \frac{A}{N_A \rho \sigma} \qquad \text{(eq. 3.39),}$$

where *A* is the atomic weight (g/mole), N_A is Avogadro's number (6.022x10²³ atoms/mole), ρ is the density (g/cm³), and σ is the cross section of the interacting molecule. It should be noted that the mean free path of an X-ray is roughly equivalent to its absorption length due to its energy being completely absorbed by the first target it interacts with. However, particles with mass (such as protons) do not get fully absorbed in the first interaction; rather it takes a number of interactions, or steps, for the energy to be fully absorbed. Typically, for a proton, this energy is 21eV per λ .

The stopping power of the proton, defined in Equation 3.38, can also be used to calculate the density of dark spikes generated for a given fluence through

$$D_{spike} = \frac{10^9 \rho SF x_{spike} D_{eff}}{E_D} \qquad \text{(eq. 3.40)},$$

where D_{spike} is the density of dark spikes (cm⁻²), x_{spike} is the depth from the siliconsilicon oxide interface where the dark spikes are formed (usually close to the surface of the CCD), *F* is the proton fluence, *S* is the proton stopping power, E_D is the displacement energy (eV), and D_{eff} is the dark spike efficiency factor, given as

$$D_{eff} = \frac{number \ of \ dark \ spikes \ per \ pixel}{number \ of \ protons \ per \ pixel} \qquad (eq. \ 3.41).$$

3.4.2.1 Reducing effects of NIEL

In a similar way to ionised radiation damaged detectors, displacement damaged detectors anneal overtime. In this case, thermal annealing can release captured acceptors or donors, preventing the detector from degrading. The annealing process can be performed manually: the lattice displacement can be repaired by cycling the detector to room temperature or higher, then back to the starting operating temperature.

The charge transfer efficiency degradation is reduced at lower operating temperatures; the CTE varies according to $exp\left(-\frac{E}{kT}\right)$, where E_T is the activation energy of the lattice traps. However, this will nullify the correction process from the annealing: temperatures higher than 30°C allow trapped charged to be released very quickly. Furthermore, operating the clocking speeds (both image and serial clocks) such that they are faster than the trap capture time can lower the chance of charge being lost during readout.

Specific detector structures/formats can be less affected by displacement damage. For instance, deep depleted CCDs (that is, those that support larger potential wells) will have a lower fraction of traps formed from the same number of protons, compared to a smaller depletion depth.

A final method of reducing the impact of displacement damage is by charge injection or flood filling the device before readout. Charge injection is the process in which a predetermined level of charge is injected into the first row (or when acquiring Raman data, the charge may be injected into a row neighbouring the Raman orders). The injected charge is used to artificially fill the traps created in the pixels, reducing the chances of electrons from the useful signal being trapped. Flood filling the device is a similar approach in which the entire device is illuminated with a flat field, causing the traps to be filled before integration of the useful signal. Both methods can significantly improve the CTE of the device (as modelled in Chapter 4).
Chapter 4

Camera System Performance Model

In Chapter 1, a case was made that Jupiter's moon Europa is a key location in the Solar System for the search for life. With compelling evidence of liquid water, nutrients, and thermal energy, the moon has become the focus of a potential NASA mission: a Europa lander (Hand et al. 2016). Analytical techniques suitable for searching for and identifying potential biosignatures on Europa, as well as characterising the habitability and analysing the geological context of the moon were described in Chapter 2. In this chapter, the materials expected to be present on Europa are detailed based on measurements from the Galileo mission, with a detailed description of how the elemental and molecular structures of the samples from the surface may have been altered due to atmospheric, geological and thermal processes theorised to occur on the moon. Knowing the material (and how it has been modified) will provide information on the expected bands a Raman spectrometer camera will likely detect and hence on the dynamic range and SNR required for the detector. The capability of Raman spectroscopy in identifying the molecules and historical biological and geological processes has previously been demonstrated using, for example, the RLS-EQM and the CIRS instrument; this is outlined in terms of the materials expected to be present on Europa.

A particularly challenging aspect of exploring Europa that will drive instrument design trade-off studies is the moon's harsh radiation environment and how it will affect various detector types. As discussed in Chapter 3, radiation damage in silicon detectors can significantly degrade the performance and efficiency of the instrument and therefore compromise the reliability and accuracy of the data acquired. A method of determining the optimum detector for a Raman instrument on a Europa lander is to characterise the detector performance under the environmental constraints and evaluate possible mitigation techniques. The work in this chapter focusses on modelling the effects of radiation damage on the detectors under particular environmental scenarios (for example varying temperature and varying radiation dose levels). The development of Monte Carlo simulation code enables the performance of the instrument to be modelled in different scenarios to determine whether the detector's reduced DR and achievable SNR post-irradiation is still suitable for a Europa lander instrument, i.e. can the data (which is expected to be acquired using the radiation damaged detector, outlined Section 4.1.1) still be used to identify the material characteristics needed to address the science goals?

4.1 EUROPA LANDER MISSION

4.1.1 Science Goals

To determine which detector is most appropriate for a Europa lander instrument, it is necessary to understand the materials expected to be present on the surface of Europa, and hence the required energy resolution and achievable SNR needed to identify such materials. The Europa Lander Study team (Hand et al. 2016) provided an overview of the three key science goals that can address the pertinent questions surrounding Europa (described in Chapter 1):

- Is life present on Europa?
- Can life be supported on Europa, i.e. is Europa habitable?
- What are the geological/thermal/chemical processes that occur on the moon?

The science questions are split into specific components: the search for life, assessment of the moon's habitability, and characterisation of the moon's context for future exploration: (see Figure 4.1). These main goals are broken down into detailed objectives, which explicitly identify the data that would need to be acquired in order to answer the top level science goals. In Sections 4.1.1.1, 4.1.1.2, and 4.1.1.3, the materials expected to be present on Europa with respect to the three key objectives are described, and the capability of current Raman instruments in identifying such materials is outlined.



Figure 4.1: An image detailing the science goals of the Europa Lander mission with Goal 1 "Life" ranked the highest priority; Goal 2 "Habitability" ranked second; and Goal 3 "Context" ranked third. (Hand et al. 2016)

4.1.1.1 The Search for Evidence of Life

Searching solely for the presence of organic compounds is not sufficient for confirming evidence of life since a number of abiotic processes also produce organic compounds. Therefore, the scientific goal for most analytical instrument suites is to differentiate the molecules that are specifically formed/altered through biological processes from those that have occurred during abiotic processes. To provide a more thorough knowledge of the diversity of these processes, it is possible to use samples from specific environments on Earth to define a framework for identifying organic biosignatures on other bodies in the Solar System. Analysis of such samples

on Earth has demonstrated that biotic processes utilise energy to synthesise unique structures and functions for molecules (of which the presence/abundance ratio can be evidential for life processes) (Summons et al. 2008). That is, the resultant structures, functions, and distribution of the molecules within a substance (as well as distribution across the body) formed during biological processes are developed specifically to satisfy the requirements for life to be supported. For example, life has adapted to the extreme conditions of high pressures, cold temperatures, and hypersaline environments (conditions expected on the surface of Europa) by generating protective biopolymers and compatible solutes (Cockell et al. 2008; Marshall et al. 2007, Rull et al. 2018). The protective materials attempt to lower the freezing point of water while protecting the biogenic molecule from high concentrations of salt, see Figure 4.2. The molecules in the high pressure, cold, and hypersaline environments typically develop thick shells and are present in clustered or organised formations in biofilms, a morphological feature detectable by a Raman instrument (Rull et al. 2018), see Figure 4.2. Typical large biopolymers and solutes include anti-freezing proteins and peptides, branched or light lipids, amino acids, and simple sugars (Rull et al. 2018) as well as other structures of life (glycine, histidine, tyrosine (Hand et al. 2016)), which have distinguishable characteristics when formed from biotic processes rather than abiotic.



Figure 4.2: A schematic illustrating how potential biogenic material on Europa will have adapted to the harsh environment (Rull et al. 2018)

However, it is not just the presence of the different structures that can provide clarity on whether biological process are occurring (or have occurred) on Europa; it is also the relative distribution of the molecule type that heavily suggests biological processes. An example of this is carboxylic acids that have been observed on meteorites (Steger et al. 2011). It is not just the presence of such material that is indicative of life, rather the specific structure of carbon numbers and chains within the carboxylic acid, as identified terrestrially (Lester et al. 2007; Steger et al. 2011).

It is possible to provide more information and confidence that the sample is biotic through the analysis of isotopic excursion. The effect of lighter isotopes reacting at higher rates (which results in the productions of such reactions consisting of a higher abundance of lighter isotopes than those seen in the reactants) is well studied for carbon, and regularly used to distinguish abiotic from biotic sources of carbon on Earth (Lollar et al. 2006). Stable carbon isotopes have a higher chance of surviving diagenesis, making it more likely to be observed than other forms of biosignature on Europa (which has a high geological perturbation environment).

The second investigation in the search for life is to observe the variety of morphology both microscopically and macroscopically, which can highly

complement the identification and characterisation of organic chemistry indicative of life. Although microscopic imaging of materials cannot provide sufficient evidence for life processes, it can be used in conjugation with spectroscopy techniques. Raman spectroscopy, as an example, can identify proteins, lipids, and other carbohydrates in the 600cm⁻¹ to 4000cm⁻¹ range (Wang, J. Lambert, et al. 2016), as well as distinguishing between numerous types and species of organisms. To have this technique combined with an imaging instrument (either microscopic and/or macroscopic) will strengthen and enhance the analysis and understanding of the composition of the target sample.

As inorganic chemicals can be used as sources of energy for life processes (i.e. as part of metabolic waste products), and can be associated with, for example, surface microbial cells, it is necessary to identify and characterise such material on Europa. As detailed in Section 1.1, it is highly plausible that the moon's ocean is a hypersaline environment consisting of silica and other materials brought up from the ocean's interaction with Europa's core (Phillips et al. 2000; Pappalardo 2010; Pappalardo 2012). Moreover, if there are microorganisms present on Europa then it is expected that they will leave fingerprints in the environment in the form of inorganic material, such as silica, salts (for example, carbonates, halite, gypsum), sulphides, and iron oxides.

Identification of the inorganic mineralogy of samples acquired from on or just below the ice, and analysis of whether it occurred from biological processes, would be significantly more compelling if combined with characterisation of the distribution of organic molecules. For example, Raman spectroscopy can detect and characterise potential biological pigments such as carotene and chlorophyll derivatives (see Figure 4.3, which shows a beta-carotene Raman spectrum obtained from a sample acquired from the Arctic). Acquiring complementary Raman data of organic molecules (such as chemical functional groups CH, C-O, C=O N-H, C-C, (Sobron et al. 2008)), as well as identification of carbon and its maturation state, Raman spectroscopy can provide a detailed understanding of the complex and structurally diverse molecular composition of the samples acquired from the Europan surface. Using such a complementary analytical technique can aid in differentiating between biotic and abiotic processes, whilst also providing information on the geological and chemical maturation of the material.



Figure 4.3: In-situ Raman detection of β -carotene pigment inside an ice core in the Artic. (AMASE-NASA-ESA expedition 2008) (Rull et al. 2018)

As described in Chapter 1, it is imperative to understand the geological and historical context of the target material. It is necessary to determine whether the environment is likely to support life processes, providing confidence (or otherwise) that the materials detected are from biotic processes. It is also important to understand the history and context of the sample, for instance:

- Assuming the target sample was collected from the surface (or just below), was it formed on the icy shell or perhaps transported from the ocean?
- Would it then have been altered by the thermal fluctuations and/or any interactions with the ice once it had reached the surface?
- How long had the material been out of the ocean?

The aim will be to determine whether the sample can be used to accurately determine the habitability of the moon and its ocean.

To acquire data that can answer these questions, samples should be collected from regions on the surface that exhibit geological characteristics formed from liquid water processes. Based on the data collected from Galileo and ground based telescope observations, potential habitable regions on (and just below) the surface have been proposed (Fagents 2003; Collins & Nimmo 2009; Greeley et al. 1998), as shown in Figure 4.4. Ridges and ridge complexes are of particular interest as they strongly imply processes with liquid water such as diapiric upwelling, perched water, eruptions, cryovolcanism, and release of water onto the surface through fractures caused by tidal stresses.



Figure 4.4: Potential habitable locations on and just below Europa's icy shell surface (shown in green) (Hand et al. 2016).

4.1.1.2 Surface Habitability

The first aim of characterising and assessing the habitability of Europa is to characterise the non-ice composition of Europa's near surface material. Such data can be used to determine whether there are indicators of chemical disequilibria and other environmental factors essential for life. As defined in Chapter 1, for a body to support life, it requires a culmination of liquid water, energy, and nutrients. Figure 4.5 identifies exemplary elements and compounds that would need to be identified to assess whether the body can support life.



Figure 4.5: An example of the compounds and elements that would be expected to be present on Europa assuming a habitable environment for life (Hand et al. 2016).

Assuming a null or ambiguous result in the search for biosignatures, assessment of the geological and chemical context can provide information for the specific landing site: for example, it would be necessary to characterise whether the lack of biosignatures is localised to the landing site or the entire ocean. Moreover, characterisation of the habitability of Europa can provide insight into the likelihood of whether or not life could have evolved elsewhere on similar bodies (geologically and/or biologically), such as on the icy moon Enceladus.

A clear indicator of extinct or extant life is the presence (or lack of) and abundances of salts, such as chlorides, carbonates, and sulphates (Pappalardo et al. 2013). Raman spectroscopy has been shown to be able to identify such compositions, specifically being able to identify the type of salt, the hydration state, and the relative abundances (Rull 2002). Raman spectroscopy can also be used to determine the salt dissolution and solidification processes (Tepavitcharova et al. 2005), providing context to the sample like the chemical and biological processes the material will have gone through. An example of an instrument demonstrating the capability of Raman spectroscopy in identifying salts is the RLS-EQM. The spectra of aqueous solutions of salts expected to be present on Europa were obtained with the ExoMars RLS-EQM (1s integration time and the detector operating at a temperature of -26°C), see Figure 4.6, which shows clearly distinguishable cation characteristics of the compound, demonstrating the instrument's ability to analyse the full spectral range for relevant ices and aqueous solutions.



Figure 4.6: Raman spectra of salts in aqueous solutions taken with the RLS-EQM instrument. Inset shows Raman spectrum of v_1 (CLO4) (credit: Rull, University of Valladolid)

The CIRS instrument has also acquired data of biomolecules and salts expected to be present on Europa. The plots in Figure 4.7 clearly demonstrate that with a spectral resolution of 4-6cm⁻¹, the CIRS instrument is capable of differentiating between various types of organic and inorganic materials. Both the RLS-EQM and CIRS instruments have been able to demonstrate how Raman spectroscopy can clearly help to infer the origin of the salts, including any alterations they may have been subject to due to Europa's exogenous environment (for example, exogenous delivery of iron and aluminium minerals would be present in the form of silicates, oxides, and sulphides (Lodders & Fegley 1998)).



Figure 4.7: high SNR Raman spectra acquired with CIRS instrument, with 4-6 cm⁻¹ spectral resolution, of diagnostic biomolecules and salts that may be present on Europa's surface (credit: Alian Wang, Washington University).

The second objective within the assessment of Europa's habitability is to determine the proximity to liquid water and recently erupted materials in the location of the lander (Hand et al. 2016). If signs of life are measured on the surface of Europa, it is necessary to understand the processes which caused the life to be present on the surface. For instance, what path would the material have taken to reach the surface (assuming it had not evolved in the ice), and how had the material been affected or supported by the ocean and moon's silicate floor. However, if no biosignatures are detected, it is necessary to confirm whether the moon and its ocean are inhabitable or simply currently uninhabited. It is expected that pockets of liquid water may be present on the surface, and even possible reservoirs of liquid water (Pappalardo et al. 2013). Seismo-acoustic measurements can determine the moon's internal structure while instruments, such as Raman spectrometers, can complement such measurements with information on the interaction of the shell material with liquid water. Cryovolcanic flows have been suggested after analysis of the low-albedo surface imaged in various locations on Europa's shell with the Solid State Imager on Galileo (Fagents 2003). Such geological activity can cause the flow of water from beneath the shell into the reservoirs. Moreover, brine zones (Head et al. 2002), dikes (Ojakangas & Stevenson 1989), and subsurface melt lenses (Sotin & Tobie 2004) are examples of other processes that can transport water to the surface.

Raman spectroscopy has been shown to be capable of successfully identifying and characterising ice and ice-water features. Rull (2002) demonstrated the technique for analysing O-O vibrations and OH librations. As demonstrated in Figure 4.6, it is necessary for a Raman instrument to have an adequate spectral response to identify the variations in such material. Moreover, Raman spectroscopy can be used to analyse the potential liquid water locations on the surface, such as in brines, by analysing the ice structure segregates in salts (Muñoz–Iglesias et al. 2012; Bonales et al. 2013). Analysis has also been performed on the influence of the salt on the OH and low frequency vibrations (Dubessy et al. 2002). Dubessy et al. (2002) demonstrated the analysis of the concentration of major geological chemical salts (such as LiCl, NaCl, KCl, CaCl₂, and MgCl₂) in aqueous solutions based on the Raman spectroscopy analysis of the v(OH) stretching vibrations of water.

4.1.1.3 Surface Properties and Dynamics

By providing characterisation information on physical properties and investigating the dynamic processes, the third science goal aims to develop the understanding of the process of the moon as well as providing context for future missions. Analysing the surface properties and processes can provide a more detailed context for the results acquired from the first two science goals. It can also provide engineering and technology boundary conditions for future rovers and landers to Europa and other icy bodies that may share similar geological processes, such as Enceladus.

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One of the objectives within this science goal is to characterise the dynamic processes of the moon's shell to understand exogenous and endogenous effects on the physicochemical properties of the surface material (Hand et al. 2016). Exogenous processes will include irradiation by charged particles (detail in Section 4.1.2) causing, for example, sputtering, and impacts resulting in overturn of material on the shell and altering the thermal properties of the surface. Raman spectroscopy can be used to characterise the processes that alter the materials, such as radiolysis. Potential modifications that can be identified by Raman spectroscopy include clathrate hydrates through the differentiation of the water molecules and vibrations of the guest molecule (Hand et al. 2006; Prieto-Ballesteros et al. 2005).

4.1.2 Environmental Constraints

As previously described in Section 1.1, Europa is known to have a high radiation environment, which can affect a mission in two ways: the radiation can modify the ratio of substances (such as sulphur) in the surface composition of the moon (Johnson et al. 2008) and can potentially significantly affect the performance of the mission instruments. Johnson et al. (2008) summarise the three most significant effects of the radiation on the moon's surface:

- Low energy magnetospheric plasma can implant plasma ions, such as iogenic sulphur, contributing to sputtering effects;
- More energetic ions (those which significantly contribute to the sputtering) are known to eject neutral ions which contribute to an ambient atmosphere on the moon, resulting in the transport of material across the surface;
- Energetic electrons and light ions are a primary source of ionisation energy that can alter the surface molecular and mineralogical chemistry.

Therefore, a detailed understanding of the Europan radiation environment is necessary to ensure that the molecular and elemental data acquired by the analytical instruments, are fully analysed and characterised with knowledge of how the Europan environment may modify the compositional structure of the sample.

It is also necessary for determining the methods of mitigating the effects of radiation on the instrument: for example, establishing the level of shielding required as well as trading off detector type and architecture with the detector performance characteristics, described in Section 3.2.2 (such as using a NIMO device which is more radiation tolerant than an AIMO device but generates much high dark current at the same temperature). The mission instruments may be affected by the harsh radiation environment, as introduced in Chapter 3 and further detailed in Section 4.1.3. Most notably, the CTE of a CCD may significantly decrease, reducing the reliability and accuracy of the data acquired. For instance, for the CIRS instrument, degradation in the CTE of the detector can cause contamination of Raman spectral orders and decrease the SNR of the device such that Raman bands cannot be detected.

The moon's orbital radius is approximately 9.39 Jupiter radii and is tilted relative to Jupiter's equator, with a slight eccentricity of 0.0094. As described in Chapter 1, the position of Europa and its orbital tilt with respect to Jupiter induces a magnetic field around the moon. However, such an orbit also significantly experiences the effect of the radiation ejected from the gas planet in its radiation belt (Hammock et al. 2009). The radiation belts and magnetosphere result in energetic electrons, heavy ions (such as oxygen and sulphur), and energetic protons being injected into the Europa atmosphere and surface. Energy spectra collected from the Energetic Particle Detector (EPD) instrument (onboard Galileo) (J. F. Cooper et al. 2001; Mauk et al. 2004; Paranicas et al. 2002) are shown in terms of intensity for specific energies of protons, oxygen, and sulphur ions in Figure 4.8 (Paranicas et al. 2009a). The data were collected from five Galileo encounters with Europa at distances ranging from 201km to 1439km away from the moon. The data show that the measurements made when Europa was positioned closest to Jupiter's magnetic equator tend to have the highest intensities at the highest energies (at flybys labelled E12 and E19) compared to those further away from the magnetic equator (at flyby E4). However, this trend is not noticeable at lower energies. Therefore, the position of Europa with respect to the planet's magnetic equator can influence the level of radiation that the instrument will undergo, and that there will be fluctuations in the level throughout the mission. Analysing the data from the EDP, Jun et al. (2005) concluded that near Europa's orbital distance, the 1σ level of the \geq 11-MeV flux is about a factor of 2 to 3 times the mean of the measurements, and the 2σ level is a factor of 10 greater.



Figure 4.8: Data of energy spectra by ion species from Galileo spacecraft encounters with Europa, data computed from (a) Cooper et al. (2001), (b) Mauk et al. (2004), and (c) Paranicas et al. (2002), collated by Paranicas et al. (2009).

To determine the fluences and doses expected for a mission to the Jovian environment, the Galileo Interim Radiation Electron model (GIRE-2) was developed (Garrett et al. 2012). Based on the EPD and magnetometer data from the Galileo spacecraft, the Jovian radiation model was developed to calculate the expected fluence levels for distances of 1.03 to 30 Jupiter radii from 1971 to 2050 (Evans & Brinza 2014). The model is dependent on spacecraft local time based on the Khurana magnetic field model (Khurana 1992; Khurana & Schwarzl 2005). Grid2, an optimised version of GIRE-2, was developed to decrease the computational time of the model (from days to minutes) (Evans & Brinza 2014). The particle fluences predicted using GIRE2, grid2, and the old grid are provided in Figure 4.9, and the total dose based on shield thicknesses are presented in Figure 4.10.

Using the results from GIRE2, Hand et al. (2016) concluded that the Europa lander would experience a total ionising dose of \sim 1.7Mrad behind 10cm Al (Si equivalent). The suggestion was made to integrate the lander instruments into a radiation vault (similar to that used on Juno, and planned for the EMFM) to decrease the total expected dose to 150krad (Hand et al. 2016). However, the Europa Lander Study Report suggests that the instruments should be radiation hardened to 300krad in order to maintain a radiation design factor of 2.





Figure 4.9: The particle fluences from the GIRE2, grid2, and old grid models (Evans & Brinza 2014).



Figure 4.10: The dose-depth curve from the GIRE2, grid2, and old grid models (Evans & Brinza 2014)

4.1.3 Detector Radiation Damage

As described in section 4.1.2, the harsh radiation environment expected at the surface of Europa will provide a significant challenge with regards to the performance of detectors during a mission lifetime. A key aspect of detector performance that is extensively affected by radiation is the CTE. Characterisation of CTE with respect to irradiation fluence levels and operation of the detector (such as operating temperature and readout speed) can provide information on the extent to which the data acquired from the Europan surface is affected (in terms of reliability and accuracy). It is also possible that the noise associated with the decrease in CTE observed in damaged devices, σ_{CTE} , will begin to dominate the instrument noise, degrading the achievable SNR, compromising the system's ability to address the science goals. The model described in Section 4.2 will be used to explore the extent of possible radiation damage and potential mitigation processes that can be employed in a detector system to reduce the degradation of the CTE.

The typical CTE of an un-irradiated device CCD47-20 (both AIMO and NIMO, back and front illuminated detectors) is 99.9999% for parallel transfer (and 99.9993% for serial transfer (e2v Technologies 2017a)), characterised using charge generated by an X-ray of a known energy (typically ⁵⁵Fe (Johnson et al. 2002)). Therefore, on a device that has not been subject to radiation damage, if a charge packet is clocked through 512 rows, it will typically lose 0.05% of the charge in the pixel by the time it has reached the serial register. However, if a detector is irradiated with a dose of ~1krad, the parallel CTE will be approximately 99.96% (Holland 1990), reduced from 99.9999% in a typical non-damaged device. That is, the same packet of charge will lose 18% of its original signal after being clocked through 512 rows. In most cases, the overall CTE will be dominated by parallel transfers as in radiation damaged detectors, the serial CTE is typically an order of magnitude higher than parallel CTE (Johnson et al. 2002).

As described in Section 3.4, a significant defect found in silicon detectors following irradiation is related to the large increase in traps in the SiO₂ interface and bulk silicon. Traps are caused by highly energetic particles displacing the atoms in the silicon lattice (the dislodged atoms may displace more atoms in a cascade effect) (see Figure 3.21) resulting in vacancies. There is a probability of the vacancies

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(which are discrete energy levels below the conduction band gap) capturing electrons from the charge packet in the pixels; and a probability that the vacancies will subsequently release the electrons at a later time (potentially after the original charge packet has been clocked out of the pixel). At least 5 different types of trap have been observed in silicon devices (Cawley et al. 2001): the most common (known as Si-E) is a phosphorus defect, at 0.44eV; an oxygen defect (known as Si-A), at 0.17-0.18eV; two di-vacancy types (V-V1 and V-V2) associated with the electrons and holes in the material at 0.39eV and 0.21eV respectively; and an unknown type. Each type of trap exhibits characteristic capture and release time constants, defined by Equation 4.1 and Equation 4.2 respectively,

$$\tau_c = (\sigma v_{th} n_e)^{-1}$$
 (eq. 4.1),
 $\tau_e = \frac{e^{E/kT}}{\sigma v_{th} N_c X_n}$ (eq. 4.2),

where σ is the electron capture cross section, v_{th} is the electron thermal velocity, n_e is the signal density, X_n is the entropy factor, E is the energy level of the trap below the conduction band, and N_c is the density of states in the conduction band, given by

$$N_C = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}$$
 (eq. 4.3),

where m_e^* is the effective electron mass. The trap capture time is much shorter than the emission times (typically they are of the order $\sim \mu s$ (Janesick 2001)) and therefore it is typically the release time constant that can affect the CTE of the device. The trap emission times for four trap types are shown in Figure 4.11 for different temperatures in the range, 153K to 300K.



Figure 4.11: Example trap release constant for the 4 known trap types across 153K to 300K.

The distribution of traps within a device is random and unpredictable such that there may be areas of high concentration of traps on some areas of the detector and not in other areas (it is possible that a single pixel will contain multiple traps) (Johnson et al. 2002). The more rows the pixel has to be clocked through, the higher the chance of losing signal as it is more likely to interact with a trap. However, a charge packet in a neighbouring column that originally acquired an equal amount of charge, and is clocked through the same number of rows, may not lose as much charge (due to passing through a less concentrated area of traps). The non-uniform distribution of defects results in a fixed pattern noise, which increases in a higher radiation environment (due to a higher number of displacements in the silicon lattice). This component of noise is known as CTE noise, and is described by the following equation:

$$\sigma_{CTE} = \sqrt{2 \times (CTI) \times N_p \times signal} \qquad (eq. 4.4),$$

where N_p is the number of parallel transfers.

As a charge packet (such as those generated from Raman bands) is shifted through the device located on the surface of the CCD is read out, the part of the event positioned closer to the serial register roughly follows the predicted Poissonian distribution curve (Johnson et al. 2002). However, traps within the silicon can cause the trailing side of the charge packet (located in the pixels further away from the serial register) to spread across a large number of pixels. In a high CTI device, the trail is typically much larger than is expected from the calculated noise (read out noise, dark current noise, shot noise, etc., see equation 4.11), due to the CTI noise dominating the noise of the system (equation 4.11). An example of the trails observed in a device that exhibits high levels of CTI is shown in Figure 4.12. In this figure, a globular cluster is imaged with a back illuminated STIS CCD (Cawley et al. 2001). The serial register is located at the top of the image (so the pixels have been clocked in the direction of the orange arrow). The stars in the first section of the image (the area closer to the serial register) appear more uniform in shape as the pixels are not clocked through as many defects in the silicon. However, the stars in the bottom section have a trail feature on one side. This feature is the effect of the electrons being captured in the traps and released at random times during the transfer of the trailing pixels. Cawley et al. (2001) determined that the CTE significantly degraded over the mission lifetime: the average number of electrons in the tails of the stars increased by a factor of ~ 10 , two years after launch, demonstrating a significant degradation in the CTE as a much larger fraction of the pixel charge was being captured (and released after pixel transfer). The trailing feature seen in this image is an effect that can be seen with Raman bands: the Raman bands can be spread along the device, potentially contaminating data from neighbouring pixels.



Figure 4.12: an image taken of globular cluster NGC 6752 using a device with a high CTI. The serial register is located at the top of the image. The selection of the image at the bottom highlights the trail effects caused by a high CTI device (Cawley et al. 2001).

As the release time constant for each trap type is dependent on the operating temperature of the device (see equation 4.2), the CTI is dependent on temperature and trap type (and trap density). A plot of CTI versus detector operating temperature is shown in Figure 4.13. Typically, the most significant trap is the Si-E type (Cheryl J Marshall & Marshall 2003) although the Si-A type is of most concern at very low temperatures (Banghart et al. 1991). The transfer efficiency significantly improves at very low temperatures (around 193K) due to the Si-E trap remaining filled (Cheryl J Marshall & Marshall 2003).

The most common trap, the Si-E trap (also known as the P-V trap), causes the most significant degradation to the parallel CTE (Janesick 2001). The charge transfer inefficiency of a trap can be written in the form

$$CTI = \frac{D_T A_{pix}RTI}{S(e^-)} \exp\left(-\frac{t_{LT}}{3\tau_e}\right) \left[1 - \exp\left(-\frac{t_{LT}}{3\tau_e} - \frac{N_Z t_{LT}}{\tau_e}\right)\right] \quad \text{(eq. 4.5),}$$

where D_T is the distance between the parallel transfers, N_Z is the spacing between the charge packets, t_{LT} is the line time between the parallel transfers, A_{PIX} is the area of the pixel, and *RTI* is the radiation trap inefficiency (the ratio between the measured CTI and predicted CTI (Janesick 2001)). The first term of Equation 4.5 describes the parameters that cause the most significant CTI for specific operating temperature and readout frequency. Equation 4.5 can therefore be re-written as (Janesick 2001):

$$CTI = CTI_{worst} \exp\left(-\frac{t_{LT}}{3\tau_e}\right) \left[1 - \exp\left(-\frac{t_{LT}}{3\tau_e} - \frac{N_Z t_{LT}}{\tau_e}\right)\right] \quad (eq. 4.6).$$

Using Equation 4.6, with an assumed CTI_{worst} of 9.9966x10⁻⁵ (Janesick 2001), the CTI value can be determined for a specific temperature. The CTI as a function of temperature is shown in Figure 4.13 for temperatures in the range 153K to 300K at three different values of t_{LT} (0.01s, 0.001s, and 0.0001s).



Figure 4.13: CTI versus detector operating temperature for three line times.

The trap constants, and therefore the trail effects (also referred to as smear), shown in Figure 4.12, are also dependent on the readout frequency of the device. If the readout frequency is faster than the average capture and release times then the electrons are more likely to be released into neighbouring pixels. However, a slower readout may increase the chance of being released back into the original charge packet before it had been clocked to the next row. As seen in the graphs in Figure 4.11, the capture time is of the order $\sim \mu s$, whereas the release time is much longer, often larger than the time taken to clock the pixels to the serial register (Cheryl J Marshall & Marshall 2003). Typically, readout frequencies of 1MHz or larger are not significantly affected by displacement damage (Cheryl J Marshall & Marshall 2003) due to the capture times being larger than the clocking speed.

When a charge packet is present in a pixel, *st* electrons will be captured by a trap and held in the pixel. If the trap release time is longer than the time between each parallel transfer, and a neighbouring charge packet is transferred into the pixel, the number of electrons captured by the trap and lost by the charge packet is described by (Hopkinson 2003)

$$s_{lost} = s_{t0} \left(1 - \exp(-\frac{t}{\tau_e}) \right) \qquad (\text{eq. 4.7}),$$

where s_{t0} is the initial number of electrons, and t is the time between each parallel pixel transfer. The ratio of the number of electrons lost to the initial number of electrons is plotted for 5 different parallel charge packet transfer times in Figure 4.14 across the temperature range 153K to 300K. If the emission time is much larger than the parallel transfer time, a higher number of charge packets can be transferred through the pixel without losing electrons, as the traps will still be filled with electrons from the first charge packet. Therefore, the CTE is not significantly degraded. However, at lower temperatures where the emission time constant is only slightly larger than the parallel transfer time, the rate of electrons being released and captured from different charge packets increases, resulting in a degraded CTE. This effect is highlighted in the curves included in Figure 4.14.



Figure 4.14: The ratio of electrons lost from a charge packet after capture by a Si-E trap (across the temperature range 153K to 300K) for 5 different times between parallel charge packet transfer.



Figure 4.15: Parallel CTI against ambient light level on a CCD47-20 after irradiation 10krad of 10MeV protons (Hopkins 2000).

However, higher background ambient light levels can lower the CTI (see Figure 4.15, Hopkinson (2000)). The improvement in transfer efficiency is caused by the electrons generated from the ambient light level filling the traps before the events are clocked through the traps. The effect of using background signal to reduce CTI can be utilised as a mitigation technique: filling the traps with other electrons (such as those from the ambient background or dark current electrons) can enable the useful signal to essentially bypass the traps and not lose as much charge. If the traps are filled with ambient and/or dark current electrons, and the detector is operated at a specific temperature such that the emission time is much larger than the parallel transfer time (Figure 4.14), the CTI can be reduced. This technique can be utilised for planetary missions: for example, ambient light is likely to be present on the surface of Europa (e.g. from Jupiter). Acquiring an image (frame) of the ambient light before acquiring the Raman data, the traps can be filled with electrons from the ambient light. Subsequently, when the charge from the Raman orders is integrated and clocked down the device, most of the traps will have been previously filled, reducing the fraction of charge lost from the Raman bands, as well as minimising the charge trail from the Raman bands.

4.1.4 Raman Spectroscopy Instrument

As indicated in Section 4.1.14.1.1 Science Goals, Raman spectroscopy is an ideal analytical technique for acquiring data that can address the top science objectives of the mission, through the identification of molecules expected to be present on Europa, and the characterisation of the surface's biological and geological evolution (through the analysis of the structure of the molecules). Therefore, it would be fundamentally important to include a Raman spectrometer in the analytical instrument suite on a Europa lander. In Section 2.1.4 the typical structure of a Raman instrument and its subsystems are described. The typical subsystems include:

- Laser (to provide a large number of monochromatic photons to the sample);
- Optical head (to focus the laser light to an appropriate spot size on the sample, and to efficiently collect the scattered Raman light from the sample);

- Filters and optics (to remove unwanted signal and to collimate the Raman signal);
- Diffraction grating (to diffract collected light into component wavelengths);
- Solid state detector (to image diffracted light);
- Acquisition and processing electronics (to convert the imaged light into a Raman spectrum).

In this chapter, the focus is on the selection and optimisation of the detector for a Raman instrument proposal to Europa. The information provided in Section 4.1 can be used to define the requirements on the detector performance for the Raman spectrometer. Specifically, identifying the materials that will be analysed (for example the diversity of an amino acid such as alanine, or salts mixed in aqueous solutions versus anhydrous salts) set out the sensitivity and resolution required for a detector. The resolution of the detector must be able to identify Raman band peaks that are located near to one another in the wavenumber offset, e.g. with a resolution of 4-6cm⁻¹ using the CIRS instrument can satisfactory identify the numerous of the alanine amino acid (see Figure 4.7). Furthermore, the SNR and dynamic range of the detector must be satisfactory to identify primary and secondary Raman band peaks, of which typical ratios are \sim 5-10% (McHugh 2018; Hutchinson et al. 2014; Malherbe et al. 2017).

As well as the energy resolution and dynamic range required for identification of the Raman bands, the detector must be optimised to minimise issues with ambient light and a high fluorescent background. Even though in the current design of the CIRS instrument the sample will be analysed inside a chamber (Wang et al. 2018), it is likely that there will be some level of ambient light from the Europa surface that will contribute to the noise in the system (i.e. as charge generated over the integration time along with the Raman signal). Unwanted signal may also occur in the form of a fluorescence background (usually observed in spectra from organic compounds). To overcome issues with the ambient and fluorescent light degrading the achievable SNR, the detector may need to have a larger full well capacity. There are also instrument modifications that can be utilised to overcome such issues; e.g. the use of a pulsed laser and short integration time to acquire Raman signals whilst reducing contaminating ambient light levels (McHugh 2018); the use of ShiftedExcitation Raman Spectroscopy to separate the fluorescence and Raman light (i.e. by shifting the Raman bonds by changing the wavelength by a small amount through changes in operating temperature).

A third constraint that defines the detector design and performance requirements is the effect the Europan radiation environment has on the operation of the detector. That is, under such a harsh radiation environment, it is possible to characterise the detectors' ability to acquire the data necessary to answer the science goals of the Europa lander mission and provide a recommendation for the optimal detector type and operating mode. If it is identified that the radiation damage significantly degrades the performance such that the detector cannot perform as required (for example, it may not be possible to differentiate between necessary Raman band peaks due to a significant decrease in sensitivity), possible mitigation approaches are evaluated, which could potentially improve the detector's performance.

To perform such analysis and to determine whether particular detector types (such as a CCD or a CMOS detector) are optimum for a Europa mission, a model has been developed to characterise the detector performance under conditions expected to be present on a Europa lander mission. The simulation will be used to predict the detector's degradation in CTE under different dose levels and various operating temperatures. The effect of the degraded CTE is then be discussed in terms of the impact on the instrument's reliability to satisfy the science goals of the mission.

4.2 MODELLING INSTRUMENT PERFORMANCE

The simulation software described here was developed in order to provide a method for investigating a large set of interrelated parameters and perform complex trade-offs based on specific instrument designs in order to optimise overall performance. The model utilises parameters from each subsystem of an analytical instrument (such as the signal source acquired by the instrument optics, background signals, and spectrometer optics) and low level camera system characteristics to simulate/replicate overall performance of an instrument design.

The instrument simulator also provides a means of exploring the effects of low level detector (CCD and CMOS) operations (including specific integration times, detector

operating temperature, clocking speeds, pre-scan clocking and detector flood filling, post scan clocking and windowing), based on detector properties such as front or back illumination, AIMO and NIMO modes, QE, and FWC. The simulation also includes the effects radiation damage: a frequent causes of performance degradation during space missions. The overall impact that these detector modes and properties have on the instrument performance depend on many parameters and are heavily influenced by the various sources of noise in the system. For this reason, the simulator operates at an individual pixel level and utilises a Monte Carlo model approach. Monte Carlo models are often used to simulate systems with many degrees of freedom that do not evolve but their end state is based on a set of random numbers generated within the simulation. Monte Carlo models account for statistical fluctuations of parameters (such as noise) that affect the overall simulation result, and is particularly appropriate for understanding the effects of traps introduced by radiation damage (as described in Section 4.1.3). The simulation produces a virtual detector image (based on the combined effect of many complex parameters) and a subsequent virtual spectrum, allowing the investigation of SNR and the overall science capability of the instrument to be investigated.

The simulation is based on 3 virtual grids: a flux grid, a charge grid, and a sample grid. The sample and charge grids contain a predefined number of elements corresponding to the number of pixels within the detector. The type of detector (and the associated size of the grids) can be modified depending on the system being investigated. The flux grid often contains the same number of elements as the other two grids, but can be extended to represent a specific input light field, such as a planetary surface, which would extend beyond the instruments field of view. Figure 4.16 shows the sequence of events that occur during the simulation with respect to the three grids.



Figure 4.16: A flow chart illustrating the inputs, sequence of algorithms, and outputs of the simulation.

Before the Monte Carlo simulations are executed, the flux grid is generated to spatially define the system input flux at the focal plane of the detector. The grid contains analytical signal, such as Raman scattered photons, UV fluorescence or X-rays. This signal is convolved to simulate the effects of the input optics of the instrument and is distributed over the flux grid according to the optical design of the instrument (for example, Raman emission bands are added to the flux grid within a narrow array simulating the diffraction order produced by the spectrometer). The scale of the convolution can be varied to account for the wide range of optical configurations analytical instruments exhibit. If necessary, the simulation also adds additional signals such as fluorescence emission, which again will be confined to a particular position on the flux grid depending on the systems optical configuration. The intensity of the analytical signals can be modified to account for the emission difference observed between samples and instrument properties such as laser wavelength and power. Figure 4.17 shows an example flux grid containing a convolved light spot. The insert highlights the intensity difference

between the centre of the spot and the outer edges as a result of the optical convolution effect applied to the flux grid.



Figure 4.17: An example of a flux grid containing a single point of light, convolved to simulate the effect of optics on the incoming light. The insert shows the variation of intensity over the grid elements.

The flux grid also contains ambient light collected by the instrument that is local to the detector, the intensity and distribution of which depends on the operating environment of the instrument. Figure 4.18 shows a CCD image containing directional ambient light of an intensity that is discernible from the background.



Figure 4.18: An example of CCD image containing directional ambient light incident on the lower half of the detector.

The example flux grid containing diffraction orders produced by the spectrograph of a Raman spectrometer is shown in Figure 4.19. Each diffraction order contains a number of Raman bands, varying in intensity. The flux grid contains low ambient light as the model was simulating an instrument contained within the main body of the rover, shielded from the external planetary environment.



Figure 4.19: An example flux grid (top) and a CCD image from the CIRS instrument (bottom) containing signal from a neon calibration source, to show similarities in optical distribution

Once the flux grid has been established, the simulation generates a charge grid (as if it was in the detector) as a consequence of the incident light from the flux grid. Initially, the charge grid is an empty array of elements (pixels), both of which exhibit a size (and format) predefined by the detector being simulated. For example, when simulating a CCD42-10, the charge grid would contain 2048 x 512 elements, each capable of storing 100,000 electrons. Depending on the detector type, the grid will be generated accounting for a number of different properties including quantum efficiency and full well capacity, which will determine the amount of charge generated in each element.

At this stage, the simulation accounts for the defects produced in the silicon due to radiation damage. To simulate the effects of proton damage, the simulation creates an array of charge traps, which is then added to the charge grid as a property that governs the charge levels in each pixel during the simulation. The density and position of traps within the trap grid are determined by the number of protons with which the detector has been irradiated, i.e. a fluence level. The traps within the array will capture and release charge in the charge array on a time scale based on their particular energy levels (trap properties described in Section 4.1.3) and temperature during the integration and readout process. An example trap grid is shown in Figure 4.20.



Figure 4.20: An example trap grid. The colour variation in the image corresponds to the number of traps in the associated pixel.

When the empty charge grid has been generated, the simulation is initiated, replicating the signal integration and readout sequence of a device. During the integration stage of the simulation, 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, additional dark current charge is added to each pixel, according to the level that the detector type (at a particular operating temperature) would produce (see Figure 4.16). The contribution of dark current at a specific operating temperature, *T*, for AIMO detectors (Equation 4.8) and NIMO detectors (Equation 4.9) are given by:

$$I_D = I_0 1.14 \times 10^6 T^3 e^{-9080/T} \quad (eq. 4.8),$$
$$I_D = I_0 122T^3 e^{-6400/T} \quad (eq. 4.9),$$

where *I*₀ is the dark current at 293K. The dark current expected for the two different detector types as a function of temperature is plotted in the graphs shown in Figures 3.12 and 3.13. 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 charge integration process. This element simulates the statistical variation observed when sampling the light incident on the surface of the detector. This is also

applied to the level of dark current generated in each pixel, simulation dark current noise. The total noise is given by Equation 4.10,

$$\delta_{pix} = \sqrt{\delta_R^2 + \delta_f^2 + \delta_a^2 + \delta_d} \qquad (eq. 4.10),$$

where δ_R , δ_f , and δ_a are the intensity of the analytical signal, the fluorescence, and the ambient light respectively, with δ_d as the dark current.

Sample grid is a representation of a digital image that would be produced by the detector (charge grid) and the readout process being simulated. The sample grid contains a number of elements corresponding the number of pixels read out during the clocking sequence, accounts for detector properties such as the serial register capacity (if applicable), number of bytes in ADC unit and system read noise.

To simulate a given readout process, a CCD readout process for example, the virtual charge is shifted down the charge grid, towards a virtual readout register. The charge in the virtual serial register is then 'read out', creating the sample grid. This process can account for pre and post-scanning/clocks, windowing and on-chip binning.

After each shift, the charge and sample grid is updated to determine the level of signal in each pixel, accounting for the build-up of dark current during read out and the accumulation of signal and ambient light. The low level algorithms are also used to calculate the status of traps within each pixel, i.e. if they have captured or released charge during the shift event. Their status is based on trap properties and how long the charge has occupied a pixel, i.e. time taken for a device to complete a parallel clock transfer sequence (see Section 4.1.3) and the time it takes to read out and digitise a row, both of which are device dependent and could be dictated by science or mission requirements. Both the charge and sample grids show the impact of radiation damage, i.e. image smearing or signal loss due to charge traps (a decrease in CTE). The effects are therefore also apparent in spectra simulated by the model. Figure 4.21 shows the vertical profile of an integrated light spot (similar to that shown in Figure 4.17) and the impact of charge trapping on the location of charge. The right-most edge of the light spot is extended due to deferral of charge to subsequent pixels during readout, which was originally in the centre of the spot. The profile demonstrates how charge deferral can decrease the signal contained within

the original pixel (i.e. the intensity of a Raman band) which will reduced the overall SNR of the acquired data.



Figure 4.21: An example profile of charge within the charge grid that has been deformed due to traps within the silicon. The additional charge in trailing pixels will also contribute to the overall pixel noise. The total noise in a given pixel within the charge grid is given by Equation 4.11:

$$\sigma_{pix} = \sqrt{\sigma_{CTE}^{2} + {\delta_{R}}^{2} + {\delta_{f}}^{2} + {\delta_{a}}^{2} + {\delta_{d}}}$$
 (eq. 4.11),

where σ_{CTE} is the charge transfer efficiency noise.

Once the charge generated by the signal has reached the serial register, the read out sequence is initiated and the sample grid is updated with the read out row. In this process the charge is converted to ADC units, applying a read noise appropriate for the system simulated. Figure 4.22 shows an example CCD images produced by the simulation (i.e. a sample grid). The image contains a number of Raman emission bands distributed over two diffraction orders. The image also contains over clocked regions and a level of background signal, composed of dark current and ambient light. This image was produced by integrating a continuous signal for 2 seconds onto a 2048 x 512 device. The device was then read out at a speed of 400kHz without a shutter (resulting in the smearing effects visible in the image). Due to the direction of the readout (downwards), the smear from the upper order will contaminate the lower diffraction order, producing artefacts that could be identified as acquired

Raman bands. This can often occur when using large devices and/or detectors with a slow readout frequency. If this operating mode was utilised by the DWARF or CIRS instruments (which produce multiple diffraction orders), during a Europa mission intense Raman bands would have the potential of contaminating the lower orders, creating additional signal peaks.

Often image smear is reduced by selecting a region of interest on the device containing useful signal. The pixels that do not contain data are shifted rapidly to the bottom of the device but are not read out. The pixels containing data are then slowly read out of the device (this is known as windowing).





Figure 4.22: An example of a simulated CCD image (sample grid). The image contains twelve Raman bands distributed over two diffraction orders.

Figure 4.23: A simulated Raman spectrum containing modelled emission bands from a neon source.

400

200

0

0

Figure 4.23 shows an example spectrum extracted from the sample grid. The spectrum was extracted by summing the pixel values in each column containing signal, and plotting the resulting profile as a function of column number.

600

Pixel no.

800

1000

The resulting sample grid and spectra can also be post processed to investigate the impact of frame stacking and data extraction techniques on the achievable SNR values (and therefore the performance) of the simulated system.

4.3 RESULTS OF PERFORMANCE INVESTIGATIONS

4.3.1 Detector Trade-Off

CCDs were first used for space applications in 1984 (for the camera that imaged Halley's comet) and have since been the predominant choice for imaging instruments (Waltham 2013). CMOS detectors have been used for space applications (for example as star trackers) since they are often more compact, and have lower mass and lower power budgets (Waltham 2013) than their CCD counterparts. However, the most significant advantage that a CMOS device has over the CCD is its inherent radiation tolerance/hardness, which is significant for missions to, for instance, Europa (where the radiation environment is particularly challenging).

Both CMOS and CCD detectors can be considered for a Raman spectrometer. Sections 3.2 and 3.3 summarise the general architectures and performance characteristics of typical CCD and CMOS devices. In light of this, this section presents a detailed performance comparison, specifically for the two detectors are described and proposed for the Raman instrument for a Europa lander mission: the CCD47-20 (a BI, NIMO CCD) and the CIS120 (a BI CMOS detector). The performance of both detectors in a Europa environment are modelled with respect to the achievable SNR (and hence ability to identify expected Raman bands). The results of the model, are used to guide the recommendation for the optimum detector for the Raman instrument.

4.3.1.1 Performance Characteristics

The CCD47-20 (e2v Technologies 2017a) is a back-illuminated, NIMO CCD detector. The device has frame transfer architecture: an image region, which incorporates 1024 x 1024, 13µm square pixels; and a storage region, which incorporates 1024 x 1033, 13µm square pixels. The device is designed for fast readout (maximum readout frequency of 5MHz) of the integrated signal into the storage region, in which they are transferred to the serial register and read out through one of two (or both) outputs. The FWC of the device is 120k electrons/pixel, and the maximum dynamic range achievable is 50,000:1. The typical level of dark signal generated at
293K is 20,000e/pix/s (compared to 250 e/pix/s for an AIMO version of the same detector). The typical parallel CTE of a non-damaged CCD47-20 is 99.9999% and the typical serial CTE is 99.9993%. A summary of the performance and functionality characteristics is provided in Table 4.1.

The CIS120 device (e2v Technologies 2017b) is a back-illuminated, digital output CMOS imaging sensor. The CMOS device incorporates 2048x2048, 10µm square pixels. The device can incorporate the 5T pixel type; with this pixel the device can use rolling shutter and global shutter modes to mitigate ambient light level and blur effects. Each row of pixels can be digitised by a separate ADC. Pixels in this device have a typical FWC of 35k electrons/pixel and a dark current level of 50e/pix/s at 293K.

	CCD47-20	CIS120
Architecture	Back-illuminated	Back-illuminated
Pixel size (µm)	13	10
Number of pixels	1024 x 1024	2048 x 2048
FWC (e/pixel)	120,000	35,000
Dark current at 293K (e/pix/s)	20,000	50
QE at 550nm (%)	85	90
Power dissipation (W)	~10	<0.35

Table 4.1: A summary of the CCD47-20 and CIS120 performance and functionality parameters (e2v Teledyne 2017a, 2017b).

Circuit

The general structure of the CMOS and CCD detectors are significantly different at the pixel level: the CMOS pixel is integrated with its own readout circuit, whereas the CCD has one circuit for the entire set of pixels. The CMOS device is simpler to drive/operate than a CCD; e.g. the CIS120 has an integrated column parallel ADC for digitisation (between 8 and 14 bits), controlled by its own sequencer. However, the CCD47-20 requires an external CDS-ADC chip and specific circuitry on the proximity board to interface both chips.

Pixel Uniformity

The independent pixel structure of a CMOS device tends to cause a large variance in sensitivity and performance on a pixel to pixel basis. As the CCD pixels are fabricated from the same mask and integrated in the same way without individual circuits, there is a significant reduction in non-uniformity across the pixels. In the CCD, the pixels may exhibit some level of DSNU and PRNU. However, the pixels in a CMOS device also exhibit non-uniformity across the pixel specific electronics/circuitry.

Dynamic Range and FWC

The CCD47-20 has a full well capacity of 120,000 electrons per pixel, 3 times greater than that of the CIS120 (35,000 electrons per pixel). In general, the CCD detector tends to have a higher dynamic range than CMOS devices due to the larger full well capacity as well as the low noise levels. The CCD read noise is only dependent on the single read out/output circuit, whereas the CMOS device has read noise associated with in each pixel. A CCD typically has a dynamic range greater by a factor of at least 2.

Quantum Efficiency

As the photosensitive areas on both the CIS120 and CCD47-20 are both designed in the MOS structure, the sensitivity to respective wavelengths does not tend to vary significantly. Both devices are available with AR coatings for optimised detection at specific wavelength ranges. For a typical Raman laser wavelength of 532nm (and expected Raman spectral range), both detectors have good QE (at 85% and 90% for the CCD47-20 and CIS120 respectively).

Responsivity

As it is easier to integrate gain circuits in the CMOS pixels than for the overall CCD, CMOS APS tend to have slightly better responsivity than CCDs. The transistors incorporated in the CMOS pixels allow low power and high-gain amplifiers to reduce effects of high impedance; in a CCD, although very achievable nonetheless, this can come at a cost to the power budget.

CTE

CMOS devices are typically more radiation tolerant than CCDs due to the independent pixel structure. As there is no transfer of charge from pixel to pixel in a CMOS APS, the degradation described in Section 4.1.3 does not occur. Although charge may be trapped in the defects in the oxide layer in a CMOS detector, the inclusion of that charge in another pixel is no longer an issue. The effect of various radiation fluences (specifically the degradation of SNR with respect to identification of Raman bands) on both the CIS120 and CCD47-20 has been modelled in Section 4.3.2.

4.3.2 Performance in High Radiation Conditions

The performance of a device can be effected significantly by radiation damage in terms of the level of dark current generated and the impact of traps on CTE. Here the effects on achievable SNR (and hence reliable identification of the Raman band peaks) under various radiation fluence levels, during operation at a range of temperatures, and for a number of different integration times were assessed. To analyse such effects in the CCD, the noise of the system was modelled as

$$Noise = \sqrt{I_D t_N N + N \sigma_r^2 + N t_N n + CTE + A_L t_N N} \quad (eq. 4.12),$$

where *N* is the number of stacked frames, and t_N is the frame time. The dark current value, I_D , for a device that has not been irradiated is determined from Equations 4.8 and 4.9 (depending on device architecture). However, for a radiation damaged device, the dark current increases as a function of displacement damage. In addition, there is also a significant increase in the DSNU (Cheryl J Marshall & Marshall 2003), resulting in a larger variance of dark current noise levels across the detector (i.e. pixel to pixel variations in dark current can become significant). Previous work has demonstrated that the increase in average dark signal level is linear with respect to total proton fluence (Srour & Lo 2000; Hubbs et al. 2005), and therefore, it was

possible to simulate the expected dark current for a range of proton fluences at specific operating temperatures.

The dark current levels for proton fluences (up to 5x10¹¹ protons/cm²) for a CCD47-20 are plotted in Figure 4.24 for temperatures of 233K, 273K, and 283K. The dark current levels for the CIS120 are shown in Figure 4.25.



Figure 4.24: Predicted dark current generation in a CCD47-20 operating at three temperatures (233K, 273K, 283K) for a range of proton fluences.



Figure 4.25: Predicted dark current generation in a CIS120 operating at three temperatures (233K, 273K, 283K) for a range of proton fluences.

Using the dark current equations (used to model the data in Figures 4.24 and 4.25), the value of *I_D* (in Equation 4.12) was derived for specific doses at across a range of temperatures, to model how the SNR of two Raman band peaks are affected. To assess the SNR variation of a primary Raman band and secondary Raman band, the simulation modelled the two detectors (CCD47-20, CIS120) operating at 233K. In both cases, the variation in achievable SNR was assessed for both a non-radiation damaged device and a device irradiated with a proton fluence of 1x10¹¹ protons/cm². The flux of the primary band was chosen to be 260k photons/s (which will take 0.1s to reach 80% FWC of the CMOS device). The secondary band flux was chosen to be 14k photons/s, providing a ratio of 5% between the two peaks (as observed in the CIO4⁻ internal vibration and d(OH) bands in the Raman spectra provided in Figure 4.6). The SNR calculations for the two peaks using the CCD47-20 are presented in Figure 4.26 and using the CIS120 are plotted in Figure 4.27. A summary of the values obtained after integration times of 1 second and 10 seconds for both bands and both detectors are provided in Table 4.2.



Figure 4.26: SNR versus total integration time for two Raman band peaks (280k photons/s and 14k photons/s) using a non-damaged CCD47-20, and a CCD47-20 irradiated with dose 1x10¹¹ protons/cm² operated at 233K (-40°C).



Figure 4.27: SNR versus total integration time for two Raman band peaks (280k photons/s and 14k photons/s) using the CIS120 operated at 233K (-40°C) irradiated with dose 1x10¹¹ protons/cm².

	CCD47-20		CIS120		
	No radiation	1×10^{11}	No radiation	1×10^{11}	
		protons/cm-		protons/cm-	
1s	31.000	2 0 2 1	22 125	22.068	
Primary peak	51,000	2,051	22,133	22,000	
10s	98165	6 4 2 3	69 999	69 787	
Primary peak	90,105	0,125	0,,,,,,	0,707	
1s	1 002	102	3 500	3,398	
Secondary peak	1,772	102	3,300		
10s	7 322	322	14 287	13 613	
Secondary peak	7,322	522	11,207	13,013	

Table 4.2: SNR calculations after a total integration time of 1s and 10s, for two Raman band peaks (280k photons/s and 14k photons/s) using an undamaged CIS120, a radiation damaged (1x10¹¹ protons/cm²) CIS120, an undamaged CCD47-20, a radiation damaged (1x10¹¹ protons/cm²) CCD47-20, operated at 233K (-40°C).

After a total integration time of 1 second, the SNR of the primary band acquired using the non-damaged CCD47-20 is \sim 31,000 and the CIS120 is \sim 22,135. Similarly, after an integration time of 10 seconds, the SNR values are \sim 98,165 and \sim 69,999 for the CCD and CMOS devices respectively.

After simulating the irradiation of the detectors with proton fluences of $1x10^{11}$ protons/cm², and calculating the increased level of dark current generation in both devices (see Figures 4.24 and 4.25) the modified achievable SNR values were assessed for both devices. For the primary band after 1 second and 10 seconds, there is a decrease in SNR by a factor of ~16, with a value of 2,031 and 6,423 respectively.

The simulation was also used to demonstrate the advantage of stacking frames to increase the SNR of the solid state detector, a process that should be considered for the detector in the Raman instrument proposed in order to increase the intensity of the Raman band whilst minimising the noise of the system. The effect of the stacking process can be seen clearly in the primary band of the undamaged CCD47-20 in Figure 4.26 (and the secondary band acquired by the CIS120 in Figure 4.27). A magnification of the primary band from Figure 4.26 is provided in Figure 4.28 to highlight the features of the frame stacking process. For the first frame (0 to \sim 0.33s), the noise increases to the power of ½. Once 80% of the linear capacity is reached, the second frame is stacked on top of frame 1.



Figure 4.28: A graph illustrating SNR increase over 2 frames for two Raman band peaks (280k photons/s and 14k photons/s) using a non-damaged CCD47-20 operated at 233K (-40°C).

The change in achievable SNR of the primary Raman band peak for varying doses was also modelled for the CCD47-20 and CIS120. The flux of 26k photons/s was

modelled across a temperature range of 183K to 303K, for 6 different proton fluences as well as for a non-radiation damaged device. The modelled values are shown in Figure 4.29 for the CCD47-20.



Figure 4.29: SNR against temperature for a Raman band peak with flux of 26k photons/s for a CCD47-20 irradiated with varying doses, integrated for 80s.

4.3.3 Instrument Simulation Results

The simulator was used to investigate the performance a CCD42-10 detector after exposure to different irradiation levels. The levels were 1x10¹², 5x10¹² and 1x10¹³ protons cm⁻². These fluences represent the dose experienced by the instrument in a 'worst-case' unshielded scenario. The simulation was used to investigate the impact of traps induced by the radiation damage and their impact on the charge transfer efficiency. The system was simulated at three different operating temperatures: 263K, 233K and 183K, in order to evaluate the impact of detector temperature as a mitigation technique for radiation damage.

To investigate the impact of different proton doses on device performance, the simulation was modified to model a light spot incident on a proton damaged detector. The flux grid generated contained a fixed fluence of 100 photons/second

distributed into a single spot. No ambient light was assumed to be falling on the detector.

The charge grid was 2248 x 512 elements (pixels) in size, with each exhibiting a FWC of $1x10^5$ electrons, while the serial register and (virtual) output node held $3x10^5$ and $6x10^5$ electrons respectively.

For each simulation run, the trap grid was modified to reflect the different trap densities that would arise from the different fluence levels. The number of traps produced by the fluence levels 1×10^{12} , 5×10^{12} and 1×10^{13} protons cm⁻² are shown in Table 4.3. The total number of traps (proportional to the fluence level) was uniformly distributed over the trap grid and therefore over the charge grid.

	Fluence (proton cm ⁻²)			
Тгар Туре	1x10 ¹²	5x10 ¹²	1x10 ¹³	
SiE	750	3750	7500	
SiA	150	750	1500	
VV1	116	581	1162	
VV2	1500	7500	15000	

Table 4.3: A summary of the number of traps produced (for each type) as a function of fluence.

The spot was integrated on to the detector at an (x,y) position of (1000, 150) for 1 second (integrated in steps of 0.1seconds. i.e. the charge grid was updated 10 times during readout. Every 0.1seconds, the level of charge was calculated with the appropriate levels of dark current (for the device operating temperature) and the status of the traps was evaluated. However, in order to investigate the extent of charge deferral, a shutter mechanism was simulated i.e. the flux grid was not integrated during readout. The charge was read out at a rate of 400kHz with a parallel clocking speed of 5kHz. In total, 300 simulations were completed for each fluence, at each temperature. The 300 sample grids were then stacked into one final image.

In order to observe the extent of the charge deferral (due to the capture and relatively delayed release of charge into a neighbouring pixel during readout) a vertical profile of the integrated light spot was extracted from the resulting sample grid. Figure 4.30 shows the vertical profile of the spot integrated onto a detector (which had been exposed to 1×10^{12} protons cm⁻²) operating at three different temperatures (183K, 233K and 263K).

Given the similarities of the profiles presented in Figure 4.30, Figure 4.31 highlights the differences on the right side of the profile.



Figure 4.30: Vertical spot profiles observed at temperatures of 183K, 233K and 263K when simulating a detector exposed to 1x10¹² protons cm⁻².



Figure 4.31: A close up of the profiles presented in Figure 4.30.

The CTE of the curves is the percentage ratio of the maximum intensity within the spot to the expected spot intensity (which without the influence of charge traps would have been ~300). The CTE for the 183K, 233K and 263K curves are 86%, 84% and 80% respectively. Figure 4.32 presents the vertical profiles of the light spot after it had been clocked through a device damaged by 5×10^{12} protons cm⁻², at three different operating temperatures.



Figure 4.32: Three spot profiles acquired at different operating temperatures after a simulated proton exposure of 5×10^{12} protons cm².

Figure 4.33 shows in greater detail the differences between the profile tails (extending through subsequently read out rows).



Figure 4.33: A close up of the profiles presented in Figure 4.32, illustrating the difference in charge deferral expected at different operating temperatures.

The CTE for the three curves produced by simulations modelling the effects of device damage from 5×10^{12} protons cm⁻² were calculated to be 61%, 62%, and 64% for the 263K, 233K and 183K respectively.

Three simulated light spot profiles are shown in Figure 4.34. The profiles demonstrate the impact of proton irradiation damage (a dose of 1x10¹³ protons cm⁻²) on charge transfer through a device, at different operating temperatures. Figure 4.35 shows a detailed view of the trailing side of the spot (pixels subsequently clocked out of the device). The CTE for the profiles was calculated to be 45%, 34%, and 22%.

Figure 4.36 shows the same spot profile (i.e. after a dose of 1x10¹³ protons cm⁻²) when dark current is included in the device model, and demonstrates the improvement in CTE observed: there is a clear difference in tail shapes, which is due to trap filling.



Figure 4.34: Light spot profiles simulated at operating temperatures of 183K, 233K and 263K, using a simulated irradiation dose of 1x10¹³ protons cm⁻².



Figure 4.35: A close up of the right hand side of the spot profiles in Figure 4.34, high lighting the difference in charge transfer efficiency as the device operating temperature is varied.



Figure 4.36: Profiles acquired at different operating temperatures with significant background noise.

4.4 DISCUSSION

4.4.1 Dark Current Curves

Figures 4.24 and 4.25 show the predicted dark current generated by the CCD47-20 and CIS120 devices respectively, operating over three different temperatures ranges. The devices were irradiated by a fluence of 1×10^{11} protons cm⁻². It is evident from the plots that there is significant difference between the dark current levels: the CIS120 produces a lower dark current in comparison to the CCD47-20. For example, the CIS120 reached a maximum of ~43 electrons/pixel/second at 283K (at fluences less than 1×10^{11} protons cm⁻², the dark current does not exceed 10 electrons/pixel/second when operated at 233K), whereas the CCD47-20 reaches a level of ~3,400 electrons/pixel/second at the same temperature and radiation dose (1×10^{11} protons cm⁻²).

In the case of the CCD47-20, when operated at 283K, the dark current levels do not decrease below ~800e-/pix/second. The plots indicate that CIS2020 generates less dark current than the CCD47-20 after irradiation levels similar to those expected on Europa regardless of operating temperature.

4.4.2 SNR

Figure 4.26 shows the predicted SNR value for two Raman bands (a high intensity primary band and a lower intensity secondary band) when acquired using an undamaged CCD47-20 and a CCD47-20 irradiated with a dose of 1x10¹¹ protons cm⁻². It is evident from the figure that the proton irradiation decreases the achievable SNR value of the detector for both the primary and secondary bands. The maximum SNR of the primary band in Figure 4.26 (achieved in 10 seconds) decreased once the detector was subjected to 1x10¹¹ proton cm⁻² of damage. Similarly, the secondary peak also exhibits a decrease in SNR after irradiation.

Figure 4.27 shows the SNR achieved (from two Raman bands) using a CMOS device after 1x10¹¹ protons cm⁻² of irradiation. The CCD detector exhibits a higher SNR for the primary band than the CMOS device, although both exhibit SNR values that would satisfy the Europa mission goals. However, the SNR values of the secondary band are twice as large when acquired by an undamaged CIS120 compared to a CCD47-20.

4.4.3 Frame Stacking

The impact of frame stacking on achievable SNR is presented in Figure 4.28. The figure shows a noticeable decrease in the SNR caused by the addition of the readout noise from the new frame, which increases the noise by a factor of \sqrt{N} , where *N* is the number of frames stacked. The signal continues to integrate in the new frame and begins to dominate the noise, until the third frame is stacked. As the signal increases proportionally with *N* and the noise increases by a factor of \sqrt{N} , the SNR increases as the frames are stacked despite the addition of the electronics noise with each frame, demonstrated in both Figures 4.26 and 4.27.

The significant decrease in SNR in the CCD was due to the substantial increase in the level of dark current generation, from 33 electrons/pixel/second at 233K for an undamaged device to 18,953 electrons/pixel/second for the radiation damaged device. However, there is an almost negligible change in SNR between the non-

damaged and damaged CIS120 devices. After 1 second, the SNR value was calculated to be 22,068 (from 22,135); after 10s the achievable SNR value was determined to be 69,787 (from 69,999). This trend is also seen in the secondary band SNR values for the CIS120. The radiation damaged CIS120 SNR values are approximately 10 times greater than the CCD47-20 values for both bands. Therefore, without methods of mitigating the significant increase in dark current in the CCD47-20, the CIS120 will achieve higher SNR values for the Raman spectrometer in the high radiation environment expected on Europa than the CCD.

4.4.4 Operating Temperature

Figures 4.29 shows how the SNR of a Raman band of a particular flux is affected by operating temperatures after varying levels of proton damage. For the undamaged CCD47-20 device, the SNR begins to partially decrease at temperatures above ~290K: at 300K the SNR had only decreased by 2.5% from 183K. In contrast, the SNR of the Raman band on a detector irradiated with the highest dose (1x10¹¹ protons/cm²) significantly degrades at approximately 240K. At 300K the SNR had degraded by 89% from the SNR at 183K.

4.4.5 CTE Curves

Figure 4.30 shows the profile of a simulated light spot, integrated onto the detector that had been irradiated using a fluence of 1×10^{12} protons cm⁻². The profile is presented for three different operating temperatures. Each profile exhibits an elongated tail on the right side of the profile, caused by charge deferral out of the pixel containing the signal data.

The plot shows little variation between the profiles as a function of temperature. However, the close up of the charge tail in Figure 4.31 shows that the tail contains more change at an operating temperature of 263K compared to 233K and 183K. The figure also indicates that at a fluence level of 1×10^{12} protons cm⁻², reducing the temperature of the detector increased the CTE by 6%.

Figures 4.32 and 4.34 show the spot profiles after being clocked through devices that have under gone increased irradiation doses of $5x10^{12}$ protons/cm⁻² and $1x10^{13}$ protons/cm⁻². Similarly to Figure 4.30, the profiles feature an extended tail caused by charge deferral. Due to the increased number of traps within the silicon, the tails observed in Figures 4.32 and 4.34 contain significantly more charge compared to those in Figure 4.30. This is also reflected in the charge transfer efficiency.

The CTE observed for the various temperatures suggest that an increase of $\sim 3\%$ in CTE is achievable when the device is cooled from 263K to 183K. Similarly, cooling a device irradiated with 1×10^{13} protons cm⁻² from 263K to 183K increases the CTE to 23%, indicating that decreasing the operating temperature has a greater mitigation effect in a higher radiation environment.

Figure 4.36 shows the spot profile once the level of dark current had been introduced. In comparison to Figures 4.30, 4.32, and 4.34, the spot exhibits a shallower profile on the right hand side, indicating that charge was transferred through the device within its original pixel, and was not deferred to a subsequent one. In this case, the traps are filled with thermal electrons as the signal charge is being integrated. This means that as the charge is clocked through the device, the traps are likely to already be filled, and are less likely to impact on the transfer of signal through the device.

4.4.6 Device Recommendation

The performance of the CCD47-20 and CIS120 devices in the expected Europa environment have been modelled with respect to the Europa science goals. Despite the smaller FWC in the CIS120 (35k electrons/pixel compared to 120k electrons/pixel in the CCD47-20), after irradiation of the proton fluence 1x10¹¹ protons/cm², the CIS120 achieves SNR values 10 times greater than the CCD47-20.

4.5 INSTRUMENT DESIGN RECOMMENDATION FOR A HIGH RADIATION ENVIRONMENT

The results of the model help to define the requirements of the detector when operating in the Europa environment. Assessment of the impact of the high radiation environment on the solid state detector has clearly demonstrated the increase in charge deferral across the columns from the Raman bands (caused by traps capturing electrons in the charge packets and releasing them after the original pixel had been clocked towards the serial register). An effect of significant charge deferral occurs when two Raman orders are imaged on the device: Charge associated with a spectral feature in the first spectral order may be captured by radiation induced traps as the charge packets are clocked towards the readout register. If the release time of the captured electrons from the first spectral order is similar to the time taken for the second spectral order to reach the pixels containing the trapped charge, there is a chance that the electrons will be released into the second spectral order (hence contaminating the signal). This effect is highlighted in Figure 4.38.



Figure 4.37: The ExoMars RLS CCD in the housing connecting the detector to the SPU.



Figure 4.38: Schematic illustrating a detector with two Raman orders being clocked down a device. A Raman band with charge captured in the radiation induced traps may contaminate the second Raman band during readout.

An approach to mitigating the cross contamination is to design the instrument such that the full spectral range is diffracted across one Raman order, similar to the camera system used on the ExoMars RLS spectrometer. The detector used is a modified version of the CCD230, see Figure 4.37, incorporating 2048x512, 15µm square pixels, aligned to acquire a full singular spectral order. In this setup, with one spectral order, charge deferral can still occur as the traps would still be present (dependent on the level of radiation of the environment), however, there is no potential risk of degrading the reliability of data from cross order contamination. However, using a wide device, such as the CCD230, requires a trade-off of the mitigation of the cross contamination against mass and volume budgets and requires good alignment to guarantee the full spectral order is imaged on the device

(if the device is slightly off-axis, a fraction of the spectral order may not be focussed onto the device).

A second possible recommendation is to use a narrower device, such as the CCD47-20, designed with 1024 columns (as opposed to 2048). However, to acquire the full spectral range, the Raman light must be diffracted into two orders. Frame transfer operation would also need to be considered: having a single order results in a fewer number of rows needing to be readout, whereas, having the two spectral orders results in twice the number of rows being readout. As well as increasing the readout time between each acquisition, the time spent reading out more rows also increases the chance of smear. Utilising the frame transfer mode (by rapidly transferring the rows with both spectral orders into the storage region, in which a subsequent the serial readout is performed) can avoid signal contaminating the spectral orders, which results in smear. However, utilising the frame transfer mode can cost more and requires a larger power budget to run both sets of parallel clocks (image and storage).

A method of mitigating the frame transfer, cross contamination, and wide detector issues is by utilising a device with two readout registers (i.e. on opposite sides of the device). The detector would need to be aligned such that the orders fall on the two separate halves of the device such that they are read out with different readout registers. Transferring the orders in opposite directions results in the data not passing through the same pixels (and hence the same traps), which ensures that electrons from the first order will not be mixed with electrons from the second order. This process is illustrated in the schematic in Figure 4.39. This method can also be performed by positioning two small (e.g. 1024x512) detectors on top of one another, and aligning the instrument to focus the two orders on separate devices. The orders can subsequently be readout without cross contamination using standard detectors (as opposed to a two register device that may cost more).

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Figure 4.39: a schematic illustrating how utilising a 2 readout register device can avoid contamination issues in Figure 4.38.

In addition to reading out the individual orders independently, it is also advantageous to reduce the number of rows that the data is clocked through before reaching the readout registers. The larger the number of rows the charge packets are clocked through, the higher the chance they will interact with traps, increasing the size of the charge deferral demonstrated in Figure 4.30. Therefore, aligning the instrument such that each order is located close to the readout register will minimise the effects of the radiation damage modelled in this chapter.

4.6 CONCLUSION

The model has been developed to simulate the effects caused to three detectors used in the Raman instrument. Various sources of light (diffracted Raman light, fluorescence, ambient light, etc.) were considered and included in a Flux Grid, which was then converted into charge in the Charge Grid. The charge value simulated was dependent on the integration time and quantum efficiency of the detector. The charge packet was subsequently transferred across the rows of pixels to be read out and converted into the respective image/spectrum.

The model was specifically adapted to assess the performance of the detector under harsh radiation environments, with specific fluences of protons expected to be present on Europa. The change in CTE, and as a result the impact of charge deferral, of the detectors was analysed with respect to the operating temperature of the camera system. The output of the model was compared to previous radiation damage studies, and successfully demonstrated observed trends, such as: average dark current levels increasing linearly with radiation dose; capture and release constants being dependent on trap type, density and temperature; degraded CTE performance at very low temperatures, with significant improvement at warmer temperatures up to approximately room temperature (beyond which the performance decreases).

Environmental parameters (e.g. operating temperature and proton dose) were varied to characterise the change in detector performance, specifically in terms of identifying molecules and chemical/biological structures expected to be present on Europa, i.e. the output of the model provided an assessment of the degradation of the Raman spectra acquired. The simulation results demonstrated that the radiation damage significantly increased the level of noise of the system (due to an increase of dark current and a higher variance of fixed pattern noise) and number of defects formed in the silicon.

A significant effect of the increase in traps demonstrated by the model was the possible cross contamination of Raman spectral orders. The charge deferral caused by the capture of electrons (and release at timescales greater than the time for one parallel transfer) resulted in electrons from the first order being released into charge packets from the second order during readout. Mitigation techniques proposed include:

• Use of a device with two serial registers at opposite ends of the device, and to readout the orders in opposite directions, which results in the signal in the two orders not interacting with the same pixels.

• Alignment of a detector such that the orders are acquired on rows near to the serial register, which results in fewer parallel transfers and a lower probability of interacting with traps (and hence losing signal).

Overall, the results of the model show that the CIS120 demonstrates the optimum performance under conditions expected to be present on Europa with SNR values 10 times greater than the CCD47-20 performing under the same radiation dose. However, utilising the mitigation methods proposed, and operating at ~233K, the achievable SNR of the detector results in Raman spectra that can be used to answer the science goals of a Europa mission. This would then enable the proposal to benefit from the significant heritage associated with CCD based instruments (described in Chapters 1 and 2).

Chapter 5

Camera System Performance in High Radiation Environments

In Chapter 3, the typical performance characteristics of a detector are described and effects caused by the two types of radiation damage: ionising damage and displacement damage. High radiation environments can fundamentally change the performance, reliability, and useful lifetime of a detector during a mission. Ionising damage (caused when high energetic particles interact with the silicon in the Si-SiO₂ interface) typically results in an increase in the holes located near the surface of the detector (due to an increase in e-h pair generation and electrons being repelled from the surface), producing a positive charge build up (C.J. Marshall & Marshall 2003). The biases applied to the detector are often affected by the flat-band voltage shift caused by the uniform positive charge build up. Another impact of ionisation damage is increased dark current associated with additional states created at the surface interface.

As described in Chapter 3, displacement damage occurs when heavier particles disturb the lattice structure creating defects in the silicon, which can capture the electrons for varying time periods (dependent on the type and density of trap and operating temperature of the detector). As modelled in Chapter 4, these traps can significantly degrade the CTE of the device (depending on the operating environment of the camera system) and the radiation can significantly increase the level of dark current generation, which results in a necessity to modify/optimise the architecture and modes of operations of the camera system (such as a device with fewer rows, a device with multiple readout registers, and/or operating at low temperatures).

As detailed in Section 4.1.2, Europa has a relatively high radiation environment, with doses of 150krad protons at the surface (Hand et al. 2016). Previous work by Hopkinson (2003) has indicated $\sim 0.15V/krad$ shifts in CCD operating voltages after irradiation. In a Europa type of environment, bias shifts of order 15V to 20V may be

anticipated, highlighting the detrimental effects such an environment can have on a detector. However, thin detector gate developments by Teledyne-e2v (D. Burt et al. 2017) have shown that minor modifications to the structure of the detector (such that the thickness of nitride and oxide layers are reduced to avoid the holes tunnelling into the nitride from the silicon) result in higher radiation hardness so the induced flatband voltage shift is $\sim 6 \text{mV/krad}$, resulting in a <1V change (manageable with standard electronics). Therefore, characterising the performance and effects of the detector to guide the design and operation of the detector is essential to ensure suitable performance (with respect to the mission goals) in such an environment.

It is necessary to convert proton dose and fluence to determine the levels of fluence expected to be experienced during a surface mission to Europa. Since the epitaxial layer of a typical detector is assumed to be a thickness of ~50 μ m, and given that a 10MeV proton (on average) loses 12keV μ m⁻¹ through silicon (and 1 rad = 6.25 x 10¹³eVg⁻¹ – where a rad is the measure of absorbed dose in a material), the energy lost by one proton passing through the epitaxial layer can be calculated. As the density of silicon is 2.33gcm⁻³, the proton will lose 6 x 10⁵ eV, then, the conversion from rads to fluence is given by

$$1 \text{ rad} = 1.2 \times 10^6 \text{ protons/cm}^{-2}$$
 (eq. 5.1).

Consequently, given that a dose of 150krad of 10MeV protons is expected on the surface on Europa, then the equivalent fluence is $\sim 1 \times 10^{11}$ protons/cm². Therefore, as detailed in Section 5.2 Detector Performance, characterisation of the degradation in detector performance with increasing fluence levels (to the mission stated level of 1 x 10¹¹ protons/cm²) was performed, such that the impact on performance with the increasing damage can be understood in detail (identifying the extent to which the increasing shielding levels will improve overall instrument performance).

The first part of the chapter describes the facility that was used to irradiate the detector to levels representative of the Europa environment (i.e. up to 1×10^{11} protons/cm²), dosimetry, and shielding process. The second part of the chapter focusses on the performance of a CCD based camera system prior to and following exposure to the Europan environmental conditions. In particular, spectra obtained from Europa analogue samples were acquired with the damaged detector. The

increase in dark current and reduction in SNR (and hence ability to identify the Raman bands) were analysed and compared to the model predictions reported in Chapter 4.

5.1 SIMULATING THE EUROPA ENVIRONMENT

Characterisation of the impact of radiation on a solid state detector (that can be used in a Raman spectrometer on Europa) was performed using the CCD47-20, shown in Figure 5.1. The solid state detector is a back-illuminated, AIMO CCD, which utilises the frame transfer mode (e.g. to avoid the effects of smearing), and has been utilised in the CIRS instrument, demonstrating successful performance as a Raman spectrometer detector. The device incorporates 1024x1024, 13µm pixels in the image region and 1024x1033, 13µm pixels in the storage region. The clocks in the image region rapidly transfer the integrated charge into the storage region, in which they are subsequently readout through the serial register (located at the bottom of the storage region) at slower speeds. The CCD47-20 pixels have a typical dynamic range of 50,000:1 and a full well capacity of 100k electrons/pixel. The dark current level expected for the AIMO device has been modelled (see Figure 5.2), and where the typical number of dark current electrons generated at 293K was 250 e/pix/s.



Figure 5.1: The CCD47-20 used for irradiation characterisation.



Figure 5.2: The dark signal level of an AIMO BI CCD47-20 across the temperature range 183K to 303K.

5.1.1 Radiation Facility

The CCD47-20 was irradiated at the Scanditronix MC-40 cyclotron at the University of Birmingham. The facility provides a beam of protons with energies ranging between 3 and 40MeV (Parker 2014). During the irradiations, the CCD was unbiased and at room temperature.



Figure 5.3: The layout of the MC40 cyclotron at the University of Birmingham.



Figure 5.4: An array of beam channels for different particle energies from the 'dees' to the irradiation room.

The configuration of the radiation facility is illustrated in Figure 5.3. The particles are accelerated in the D-shaped regions ("dees") in the cyclotron vault. The proton beam is produced by ionising hydrogen gas and passing it through to the centre of the cyclotron, into the dees. Normally, two dees are used in a cyclotron; however, at the University of Birmingham facility, the dees are split in half resulting in a four quadrant cyclotron (see location (a) in the cyclotron vault room in the diagram in Figure 5.3). A magnetic field is then applied across the four quadrants; as the mass of the particle and radius of the dees are known, selecting a specific magnetic field will result in the proton beam accelerating to a specific speed, as described by the equation:

$$v = \frac{qr|B|}{m} \qquad \text{(eq. 5.2)},$$

where q is the charge of the particle of mass, m, accelerating in a radius, r, in a magnetic field of magnitude |B|. Once the proton beam has been accelerated to the appropriate speed, it is then passed through a set of magnets (see location (b) in Figure 5.3). The magnets are used to resize and reshape the beam if necessary. The beam originally exits the dees with a diameter of approximately 1mm. The

generation and acceleration of the proton beam is a continuous process; a Faraday cup inserted into the beam line is used to stop the flow of the protons to the target room when breaks are required in irradiation (for example changing the devices that are to be irradiated) without stopping the full cyclotron process.

The high energy proton beam is then directed through a beam channel that is selected based on the energy of the particles and the location of the experiment (i.e. in which part of the target room the object is to be irradiated), see Figure 5.4 and location (*c*) in Figure 5.3. For higher energy experiments, aluminium foil is used in the setup to improve uniformity of the beam over a large area. However, the foil was not effective for proton energies as low as 10MeV; instead the beam was defocussed to provide approximate uniformity. The beam subsequently can be directed through to two different locations in the target room, either a shielded region, which is used for high dose damage studies, or an unshielded region, used for low dose damage experiments. In this case, the low dose damage region was used (see (d) in Figure 5.3). The setup of the channel exit and detector to be irradiated is shown in Figure 5.5. The distance between the channel exit and the detector was set so that the beam was appropriately focused.

Before irradiating the sample, the beam is directed into an ionisation chamber with a 2.4mm air gap to measure and confirm the fluence level. There is a fixed relationship between the ionisation generated in the thickness of the air and the number of protons transmitted for a known proton energy. The aim was to irradiate the CCD47-20 with 10MeV protons. However, as the radiation facility is not in a clean environment it was necessary to keep the glass cover on the detector to avoid contaminating the silicon in the imaging area. The protons lose energy whilst travelling through the glass and hence irradiating the detector with 10MeV protons would result in protons of a lower energy interacting with the active area in the CCD. Therefore, a higher proton energy was used to irradiate the detector to confirm 10MeV protons interacted with the silicon: with the thickness and specific type of the glass (borosilicate) the energy necessary was 14MeV (the stopping power of the 14MeV proton in borosilicate is 26.6cm²/g, resulting in a loss of 4MeV through the thickness of the glass).

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Figure 5.5: The proton beam used to irradiate the detector. The beam can be focussed by varying the position of the equipment (an example of the repositioning is shown in Figure B).

5.1.2 Dosimetry

Before the detector was irradiated, dosimetry was performed to determine the uniformity of the output photon beam. A piece of Gafchromic film was placed in the beam line at the same distance that the detector was to the exit of the beam channel. One of the dosimetry patterns obtained during the radiation campaign is shown in Figure 5.6. The dark blue pattern on the film illustrates the area of the beam which is highly uniform, and some slight blurring towards the edges indicates where the intensity gradually drops off.

The profile of the intensity of a cross section taken from the middle of the beam spot is plotted in Figure 5.7 (the inset on the figure shows the location of the cross section, i.e. the point at which the profile was extracted from the beam spot). The most uniform location on the beam (a circle of radius of \sim 7.2mm from the centre of the beam) varies in intensity by 3.6%. The beam profile drops off at the edges of the circle at a rate of approximately 20% per mm. The uniformity of the beam was defined as the section of the beam within the 5% of the drop-off curve (shown in Figure 5.7), i.e. the 95% height matches the area required to ensure that all of the detector area was within the uniform region. This 95% equates to a diameter of 24mm



Figure 5.6: Photographic film irradiated with the proton beam showing the distribution of the beam.



Figure 5.7: Profile intensity of 1 pixel width cross section of the beamline irradiated on the Gafchromic film. (Inset demonstrates location of cross section). The detector was placed in the beam, within the top 95% of the shoulders of the curve to ensure uniformirty.

5.1.3 Shielding

To characterise the performance of the detector at different levels of radiation dose, aluminium shields were used to constrain the number of protons delivered to spatially separated regions of the device. The shields were constructed so that only part of the detector imaging area of the detector was visible to the proton beam for different dosage levels. However, the shields had to be manufactured to an appropriate thickness to prevent exposure of the high energy protons to the masked areas. The plot in Figure 5.8 shows the range through aluminium exhibited by protons of a specific energy. Using these data, a shield thickness of 2mm was selected for the 10MeV protons.



Figure 5.8: The depth that a proton passes through aluminium for energies ranging from 1 to 100MeV.

Photographs of the 2mm thick aluminium shields are shown in Figure 5.9. The windows were constructed such that the irradiation could be performed by adopting an incremental approach. The imaging area of the device was subjected to 3 different proton fluences: 3.0×10^{10} , 6.0×10^{10} and 1.0×10^{11} protons/cm² at 10MeV proton energy, see Figure 5.10. Initially, the shield with the largest window was placed on top of the detector and a fluence of 3.0×10^{10} protons/cm² was delivered to the surface of the detector. This first shield was designed to cover a quarter of the

imaging area of the detector protect a quarter of the imaging region (i.e. no radiation was presented to this region) (region (d) in Figure 5.10). This region was shielded in order to provide a calibration region for post irradiation characterisation tests. During the next phase of the irradiation, a second shield was placed on top of the detector to cover part of the originally irradiated region (region (a) in Figure 5.10) and another $3.0x10^{10}$ protons/cm² fluence was delivered to the detector. This resulted in the right most regions being irradiated to $6.0x10^{10}$ protons/cm² (regions (b) and (c) in Figure 5.10). In the final stage of irradiation, the third shield was placed on top of the device, which only exposes the right most quarter of the irradiated imaging area to a $4.0x10^{10}$ protons/cm² fluence, resulting in a region damaged by a total fluence of $1.0x10^{11}$ protons/cm² (region (c) in Figure 5.10). An image of the shields positioned on the detector is shown in Figure 5.11.



Figure 5.9: The different layers of aluminium shielding used to irradiate the image area of the CCD47-20 at varying levels of fluence.



Figure 5.10: Schematic of radiation damaged regions (with total fluences) on CCD. The dark shaded areas are shielded from the irradiation (including a quarter of the imaging area for post irradiation characterisation tests).



Figure 5.11: The detector and a shield positioned in front of the proton beam.

5.2 DETECTOR PERFORMANCE

5.2.1 Experimental Details

The detector performance was characterised in two separate experimental configurations: an ambient environment in which room temperature tests could be readily performed before and after irradiation (Section 5.2.1.1), and a vacuum environment (Section 5.2.1.2) in which the detector could be cooled down to temperatures as low as 183K. In both setups, the CCD47-20 was integrated into a proximity board that was specifically designed to incorporate a flex-rigid cable for thermal isolation and flexibility (see Figure 5.12). The detector was located in the PCB socket in the left of the image in Figure 5.12. A CDS-ADC chip was also located on the proximity board along with bias filter circuits and clock routing circuits. The proximity board was powered and controlled by an external electronics box, which incorporated the FPGA (which generated the biases and clocks required to drive the detector). The enclosure also incorporated the power supply, a trigger generator for shutter controlling, the temperature controller/monitor, and a Gigabit Ethernet connector.



Figure 5.12: The proximity board for the CCD designed with a flex cable for thermal isolation and movement of the detector.

5.2.1.1 Ambient Environment

The RLS prototype (developed at the University of Leicester) was used to assess the performance of the detector before and after the irradiation campaign (full details are provided in Section 2.1.4). The setup includes (see Figure 5.13):

- Excelsior DPSS 532nm laser;
- Kaiser Optical Systems MultiRxn Probe (used to focus the laser onto the sample and collect scattered light);
- Fibre optics to direct the light through the instrument;
- Notch filter to remove >99% of elastically scattered light (McHugh 2018);
- Kaiser Optical HoloSpec spectrograph (consisting of a collimating lens, holographic diffraction grating, and a moveable camera lens used for focussing);
- Detector:
 - CCD47-20;
 - Starlight Xpress, a commercial off-the-shelf CCD used for setup calibration and alignment, and context imaging.



Figure 5.13: Subsystems integrated in the RLS prototype used to characterise the CCD47-20 in an ambient environment.
5.2.1.2 Cooling Environment

To measure the performance of the CCD47-20 across a range of temperatures, the detector was integrated inside a vacuum chamber, see Figure 5.14, in which the temperature was cycled through the range 183K to 298K in steps of 10K. Temperatures above 213K were attained (and stabilised) using a TEC while liquid nitrogen was used for colder temperatures (along with a heater for stabilisation). The detector was thermally coupled to a copper heat sink (shown in Figure 5.15), which in turn was coupled to the copper flute located in the liquid nitrogen container, used when operating the detector at lower temperatures. The detector temperature was monitored using PRTs bonded to the ceramic package of the detector and controlled using a Vuemetrix thermal controller. A spectrograph was placed in front of the chamber window in order to focus the diffracted Raman light onto the detector. The position of the detector within the chamber (with respect to the window), and the width of glass window, were accounted for to ensure the diffracted light was imaged at the focal point of the spectrograph. Ten images were acquired at each step of the thermal cycle with an integration time of one second.



Figure 5.14: Setup of detector with vacuum chamber and spectrograph.



Figure 5.15: Inside the vacuum chamber, showing the copper heat sink, which was attached to the CCD47-20 for cooling to temperatures down to 183K.

5.2.2 Pre-Radiation Results

To characterise the CCD47-20 in terms of achieving the science goals for a mission to Europa, the levels of dark current generated and the detector's achievable SNR were assessed. To perform this characterisation, a number of dark frames were acquired to characterise the detector/system noise of and, subsequently, Raman spectra were acquired using the camera system (in the setup described in Section 5.2.1.1). Samples were specifically chosen to demonstrate the range of Raman band ratios expected to be present on the surface of Europa (Section 4.1) and energy resolution required to be imaged by the detector, to demonstrate that the device is capable at differentiating between the different types of a material (e.g. aqueous v anhydrous).

5.2.2.1 Dark Current Analysis

As modelled in Section 4.3.2 the level of dark current generation is expected to increase linearly with proton dose and an increase in the number of dark spikes will be observed (i.e. there will be broader DSNU distribution levels). Therefore, the dark current and number of dark spikes present in the undamaged CCD47-20 were assessed prior to the irradiation process in order to provide comparable characterisation data before and after irradiation. The dark frames were acquired using the prototype spectrometer (see Section 5.2.1.1). The instrument, located in a dark facility at room temperature, was operated in an enclosure to ensure no ambient light was imaged by the detector. One of the dark frames acquired is shown in Figure 5.16. By measuring the variance in ADU values in small ROIs (10x10 pixels) and subtracting the read noise (measured by averaging the ADU values in the underscan region of the image), the average dark current value was determined to be 3.2ADU, equivalent to \sim 58 electrons (calculated using the gain and responsivity of the camera system). The value measured is typical of the CCD47-20 at 293K (according to manufacture specifications - see e2v Technologies 2017), see Figure 5.2. The standard deviation of the average dark current was determined to be \sim 1ADU. A histogram illustrating the pixel to pixel deviation in dark signal is provided in Figure 5.17.



Figure 5.16: Dark image acquired with the CCD47-20 (no ambient light).



Figure 5.17: Histogram of the pixel intensities (dark current electrons) in the dark image acquired by the undamaged CCD47-20 at 293K.

5.2.2.2 Spectral Analysis

A calcite and a cyclohexane sample, and a neon calibration lamp were analysed using the 532nm laser RLS prototype, described in Section 5.2.1.1. The calcite sample was chosen to demonstrate the energy resolution of the CCD47-20, which can be used to identify Raman bands when fluorescent noise is present. As described in Section 4.1.1, fluorescence (which typically occurs from organic samples) is expected to be present during Raman analysis of materials from Europa. Therefore, the SNR of the detector must be high enough such that the Raman data can be reliably differentiated from the fluorescence background. An image of the Raman order acquired from the calcite sample is provided in Figure 5.18, and the corresponding spectra is shown in Figure 5.19. The cyclohexane sample and neon calibration lamp were analysed as examples of a substances with large ratios between the Raman bands. The achievable dynamic range of the detector must be sufficient to identify the Raman bands of varying intensities. An image of the two Raman orders observed with the cyclohexane sample provided in Figure 5.20, neon in Figure 5.22, and the spectra of the two orders are plotted in Figure 5.21 and Figure 5.23 respectively.



Figure 5.18: Image acquired of the Raman signal from the calcite sample.



Figure 5.19: Spectrum acquired of the Raman signal from the calcite sample.



Figure 5.20: Image acquired of two Raman orders acquired from the cyclohexane sample.



Figure 5.21: Spectra acquired of the Raman signal from the cyclohexane sample; a) from the top order in Figure **5.20**, b) from the bottom order.



Figure 5.22: Image acquired of two Raman orders acquired from the neon lamp.



Figure 5.23: Spectra acquired of the Raman signal from the neon lamp; a) from the top order in Figure **5.22**, b) from the bottom order.

Sample	Calcite	Cyclohexane	Neon Lamp	
Highest Raman				
Signal	16,493	30,472	21,140	
(electrons)				
Fluorescence Noise	106	16	12	
(electrons)	100	10	15	
Ambient Noise	69	80	73	
(electrons)		00	10	
Dark Current	72	78	77	
(electrons)				
Read Noise	36	30	40	
(electrons)	50	55	40	
Total Noise	150	120	114	
(electrons)	150			
Highest SNR	110	254	267	

Table 5.1: A summary of the SNR values (and breakdown of noise sources) calculated for the calcite and cyclohexane

 samples and neon lamp acquired at 293K with the CCD47-20.

The highest achievable SNR values for the calcite, cyclohexane, and neon spectra were calculated using the highest Raman bands. The noise values were assessed using ROIs (size 10x5 pixels): the read noise values were acquired from the underscan region; the dark current and ambient light from the main imaging area (away from the Raman orders); and the fluorescence noise values were determined from the fluorescence light between the Raman bands. The noise types and calculated SNR values are summarised in Table 5.1. The fluorescence noise dominates the SNR in the calcite spectrum (very low fluorescence was measured in the cyclohexane sample). As all spectra were acquired using the same camera system setup in the same location and operated at the same temperature, the read noise, dark current, and ambient light are similar for each of the samples. The resultant SNR values were 110 for the calcite sample, 254 for the cyclohexane sample, and 267 for the neon calibration lamp. The largest ratio between band heights in the top cyclohexane spectrum (spectrum (a) in Figure 5.21) is 8 (i.e. the smaller band is 12% of the intensity of the larger band), and 6 (the smaller band is

18% of the larger band) in the bottom spectrum (spectrum (b) in Figure 5.21). The largest ratio between the peaks in the neon lamp spectra is 7 (the smaller band is 15% of the larger band). The spectra clearly confirm the pre-irradiation detector has sufficient dynamic range and sensitivity to enable primary and secondary bands of cyclohexane to be simultaneously characterised (with typical integration times of 0.5 seconds).

5.2.3 Post Radiation Results

5.2.3.1 Dark Current Analysis

The performance of the CCD47-20 post irradiation was initially characterised by acquiring dark frames at various detector operating temperatures (using the vacuum chamber facility, see Section 5.2.1.2) and comparing to the dark current analysis performed prior to the irradiation (see Figure 5.16). An enclosure was placed around the vacuum chamber to ensure there was no ambient light was present during acquisition. A typical dark image (acquired at 297K) is shown in Figure 5.24. This image clearly shows the regions on the detector that were irradiated with the 3 different proton fluence levels (and undamaged region). There is clear spatial separation and different mean levels of dark current for each of these regions. Three more example dark images acquired at 283K, the middle at 273K, and the bottom image at 233K.



Figure 5.24: A dark image acquired at 297K highlighting the damaged regions on the detector. The colour table representing the pixel intensity is shown (white representing the highest intensity).



Figure 5.25: Three dark images taken with the CCD47-20 at 283K (top), 273K (middle), and 233K (bottom). The colour table representing the light intensity is next to the top image (white representing the highest intensity).

The individual damaged regions in the detector are clearly visible in the top image in Figure 5.25 (taken at 283K): the highest intensity region in the image is located on the left (where the dose applied was 1×10^{11} protons/cm²). The undamaged region is located on the right of the image. The contrast in intensity across the image

is caused by the increase in dark current within each region. The average dark current (in ADU) observed in a small ROI on the imaging area of the detector (10x5 pixels in each of the four regions) is listed in Table 5.2 (the read noise was determined from the underscan region).

Region	Dose	Average Dark	
	(p/cm ²)	Current (electrons)	
283K Region 3	1x10 ¹¹	4,913	
283K Region 2	6x10 ¹⁰	4,032	
283K Region 1	3x10 ¹⁰	3,112	
283K Undamaged	N/A	526	
273K Region 3	1x10 ¹¹	2,500	
273K Region 2	6x10 ¹⁰	1,595	
273K Region 1	3x10 ¹⁰	1,101	
273K Undamaged	N/A	203	
233K Region 3	1x10 ¹¹	6	
233K Region 2	6x10 ¹⁰	5	
233K Region 1	3x10 ¹⁰	3	
233K Undamaged	N/A	2	

Table 5.2: Average dark current levels for each region on the detector at 3 different temperatures (283K,273K, 233K).



Figure 5.26: The simulated increase in dark current for 283K, 273K, and 233K for the CCD47-20, for the three fluences used to irradiate the detector (purple lines).

Using the model described in Chapter 4, the dark signal expected for an AIMO CCD47-20 at three separate temperatures were determined for the proton fluences delivered to the detector. Figure 5.26 shows the predicted dark current increase for the specific fluence levels. As predicted, the increase in dark signal at lower temperatures is small. However, as expected dark signal levels do increase linearly with fluence. A plot showing the variation in dark signal with temperature for the three temperatures is provided in Figure 5.27. On each plot, the modelled dark current values are included for comparison with the measured values.

Using the dark image acquired at 293K, the variance in dark current in each irradiated region and the number of dark spikes were analysed (to compare to the analysis performed prior to the irradiation, see Section 5.2.2.1). A histogram for each region is provided in Figure 5.28. Compared to the measured dark current value of 58 electrons for the undamaged detector, the values (listed in Table 5.3) provide the dark current values and standard deviation calculated for the four regions of the radiation damaged detector. The values observed dark current increase by a factor of \sim 4 for a fluence of 1 x 10¹¹ protons/cm² (the average dark

signal level in the undamaged region remains effectively the same as the level observed before radiation). As expected from the defects caused by radiation damage (e.g. increase in dark spikes and DSNU), there is a greater variance in dark current at the higher doses compared to the levels observed for the undamaged detector (and full shielded region after irradiation). The histograms also highlight this increase in defects in comparison with the histogram shown in Figure 5.17.

	Average dark current	Standard deviation	
	(electrons)	(electrons)	
Pre-irradiated detector	58	19	
Undamaged region	62	18	
3 x 10 ¹⁰ protons/cm ²	129	55	
6 x 10 ¹⁰ protons/cm ²	174	44	
1 x 10 ¹¹ protons/cm ²	215	75	

Table 5.3: The average dark current signal and standard deviation of the undamaged detector and the four regions

 on the damaged detector, both acquired at 293K.



Figure 5.27: The average dark current values measured in the acquired dark images for 283K (top), 273K (middle), 233K (bottom). The predicted values (calculated using the model in Chapter 4) are also included.



Figure 5.28: Three histograms of the dark current levels in the three irradiated regions of the image in the dark image acquired with the irradiated CCD47-20 at 297K.

5.2.3.2 Spectral Analysis

To assess the performance of the CCD47-20 after irradiation, analogue samples expected to be present on Europa were analysed. The sample analysed included sulphur, an element expected to be present on Europa. A neon calibration lamp was also used to analyse the SNR and dynamic range of the detector (i.e. the ability to simultaneously characterise primary and secondary Raman bands, results which were compared to the undamaged detector analysis of the neon lamp spectra).

Sulphur spectra were obtained from the sulphur sample in the ambient setup using the 532nm RLS prototype system, described in Section 5.2.1.1. The two Raman bands of sulphur with the highest intensity ($221cm^{-1}$ and $475cm^{-1}$ (Rruff IDR050006)) were imaged within each of the regions of the irradiated CCD47-20 device (i.e. the spectral order was sequentially shifted across the device). The aim of this process was to demonstrate successful spectral acquisition using the irradiated detector at each of the three different proton fluence levels. For each acquisition, the detector. In Figure 5.29, the Raman bands were aligned in the undamaged region of the detector in image in Figure (1); in Figure (2) the bands were moved into the first region ($3 \times 10^{10} \text{ protons/cm}^2$). The bands were fully positioned in the second region ($6 \times 10^{10} \text{ protons/cm}^2$) in Figure (4), and in region $3 (1 \times 10^{11} \text{ protons/cm}^2)$ in Figure (6). It should be noted that in images (2) to (6), some laser light is visible (this is useful for confirming calibration and useful for investigating the effects of pixel saturation / blooming).

The spectrum extracted from Figure (1) in Figure 5.29 is provided in Figure 5.30, where the two bands are clearly be identified (at pixel numbers 829 and 1000). The spectrum clearly shows the significant increase in background noise across the regions (which increase by a factor of ~1.5 between the undamaged region and region 1, a factor of ~2 between the undamaged region and region 2, and a factor of ~2.4 between the undamaged region and region 3). The spectrum also demonstrates a significant intensity fluctuations associated by the spikes generated from the radiation. The frequency of spikes (i.e. dark signal level that is more than 3σ above the mean level) increases by a factor of ~80 in the highest irradiated region (i.e. region 3 compared to the undamaged region).

Subsequently, the bands were aligned to be present in the respective regions of the device. The bands were not identifiable in the spectra when the peaks were located in the damaged regions due to the significant number of spikes and variance in noise, which were at a significantly high level due to the operating temperature of the detector. However, as demonstrated by the acquisition of spectra from a neon calibration sample when the detector was cooled, bands can be identified in the damaged regions. The spectrum extracted from Figure (4) in Figure 5.29 has been provided in Figure 5.31, in which the Raman bands were aligned to be present in region 2. The laser light is identifiable in region 2 at pixel 659. The dominant source of noise will be the increased dark current generated due to the radiation damage. The sulphur spectra were acquired at room temperature, and as demonstrated in Section 5.2.3.1, the levels of dark current are expected to be significantly higher in all three damaged regions. From these data it is clear that the spectra are readily discernible at temperatures below (and including) 233K, see Figures 5.33, 5.34, and 5.35.



Figure 5.29: Sulphur spectra acquired with the CCD47-20 (at room temperature). The Raman band peaks were aligned in the different radiation damaged regions of the detector (the left side of each image is the highest radiation damaged).



Figure 5.30: Sulphur spectrum cross section from the image 1) shown in Figure 5.29. The spectrum is split to highlight the four different areas on the irradiated CCD.



Figure 5.31: Sulphur spectrum cross section from image 4) in Figure 5.29.

The neon lamp analysis was performed at cold temperatures (i.e. using the vacuum chamber) in order to assess the performance of the irradiated CCD47-20 across a range of temperatures, see Section 5.2.1.2 for details of the setup. The diffracted neon light exiting the spectrograph is shown in Figure 5.32. This light was aligned to the surface of the detector such that the full spectral range of the orders could be

imaged by the CCD47-20. The temperature of the chamber was stabilised using liquid nitrogen and heater resistors (for temperatures between 183K and 283K). The images acquired at 283K, 273K, and 233K are shown in Figures 5.33, 5.34, and 5.35 with their respect plotted spectra.



Figure 5.32: The diffracted neon light from the neon calibration lamp.



283K

Figure 5.33: Image of the diffracted neon lamp acquired with the irradiated CCD47-20 at 283K. The spectrum extracted from the Raman order is plotted below the image.



Figure 5.34: Image of the diffracted neon lamp acquired with the irradiated CCD47-20 at 273K. The spectrum extracted from the Raman order is plotted below the image.



233K

Figure 5.35: Image of the diffracted neon lamp acquired with the irradiated CCD47-20 at 233K. The spectrum extracted from the Raman order is plotted below the image.

Temperature	283K	283K	273K	273K	233K	233K	
	Primary	Secondary	Primary	Secondary	Primary	Secondary	
	Band	Band	Band	Band	Band	Band	
Highest							
Raman Signal	61,364	30,546	61,472	28,728	52,428	20,363	
(electrons)							
Fluorescence	102						
Noise				95	78		
(electrons)							
Ambient	334						
Noise			325		322		
(electrons)							
Dark Current	4,897		2	120		Λ	
(electrons)			2,439		4		
Read Noise	33		34		30		
(electrons)			54		50		
Total Noise	4.010		2	162	2	000	
(electrons)	4,	4,910		2,403		333	
Highest SNR	12	6	25	12	158	61	

Table 5.4: A summary of the SNR values calculated of the primary and second bands in the neon lamp spectra in the highest dose region (1 x 10¹¹ protons/cm²) of the CCD47-20. A breakdown of the noise sources are provided.

The spectra plotted in Figures 5.33, 5.34, and 5.35 confirm the ability of the radiation damaged detector to identify the key Raman bands in the neon lamp spectrum. The bands are located in region 3, the highest dose region, and are still clearly identifiable in the spectra at 233K, 273K, and 283K. The SNR values for the primary (most intense Raman band) and secondary Raman band at the three temperatures are provided in Table 5.4. The breakdown of the different noise contributions is also provided in the table. The SNR values for the primary band were determined to be 12 for the peak at 283K, 25 at 273K, and 158 at 233K. The SNR values for the secondary band were determined to be 6 at 283K, 12 at 273K, and 61 at 233K. The significant increase in SNR with decreasing temperature is due

to the significant decrease in the level of dark signal. The measured dark signal in the images (4897, 2439, and 4 electrons at 283K, 273K, and 233K respectively) are in close agreement with the predicted values the model simulated (see Figure 5.27). The significant variation in the level of dark signal at the three different temperatures is visible in the neon lamp spectra, most notably in Figure 5.33. The underscan and overscan pixels are located at pixel numbers 1 to 51 and 1054 to 1104 respectively. The increase in intensity outside of these regions are clearly identifiable in the spectra where the background noise in pixels 52 to 1053 are increased by an offset than decreases as the temperature cools. However, unlike with the sulphur spectra, the neon spectra are identifiable in the highest dose region despite the significantly high level of dark current at 283K.

5.3 CONCLUSION

In Chapter 4, a model was developed to simulate the performance of a solid state detector when subject to typical Europa environment conditions (i.e. a high radiation environment). In Chapter 5, a detector was demonstrated as being able to acquire Raman data, and subsequently subjected to irradiation to assess the effects of the radiation damage on the detector, and to demonstrate the validity of the model.

The CCD47-20, a back illuminated, AIMO detector that utilises the frame transfer operating modes was used to acquire Raman data from representative Europa samples. The detector clearly demonstrated good performance and successfully imaged the diffracted Raman light, with an SNR value of 267 for an integration time of 0.5 seconds. The Raman spectra analysed demonstrated that the detector dynamic range is capable of identifying molecular information, including high Raman band ratios and Raman bands over a high fluorescence background.

The detector was subjected to irradiation using the Scanditronix MC40 cyclotron. Three fluences of 10MeV protons were delivered to the detector: 3×10^{10} protons/cm², 6×10^{10} protons/cm², and 1×10^{11} protons/cm², the final dose representing the expected proton dose on the surface of Europa. Aluminium shields were constructed to protect the parts of the device which were not being assessed

for radiation damage from the protons, and uniform distributions of the fluences were successfully delivered to three regions on the imaging area of the detector.

Initial characterisation of the radiation damaged detector confirmed the validity of the model: the levels of dark current generation increased linearly with proton dose, as simulated in Chapter 4. The values of dark current for the temperatures at which the detector was characterised were within the predicted values for each dose (generated by the model).

A sulphur sample and neon lamp were used to analyse the performance of the radiation damaged CCD47-20 for generating Raman spectra. Both of the sets of spectra obtained clearly demonstrate the significant level of dark current increase at the respective dose levels. The dark current noise significantly degraded the SNR values achievable with the CCD47-20. However, this effect was mitigated at lower operating temperatures, as demonstrated by the acquisition of the neon lamp spectra at 233K, where the SNR was calculated to be 158 compared to the SNR of 12 at 283K (i.e. pre-irradiation levels of performance were achieved by cooling the detector to 233K). The dark current contribution was negligible at 233K temperature and the achievable SNR values measured in the highest dose region of the imaging area compared to the SNR values calculated on the non-damaged device.

Consequently, the tests performed on the radiation damaged detector clearly showed the ability of the CCD47-20 to acquire Raman spectra after irradiation of proton fluences similar to the Europa environment. It is recommended that to mitigate the significant effects of the high dark current levels generate due to the radiation damage, the detector should be operated at cooler temperatures, such as 233K. At this temperature, SNR values can be achieved which are suitable for acquiring the data necessary to adequately address the science goals of the mission.

Chapter 6

Development of a Combined Analytical Instrument for Planetary Exploration

In Chapter 4 the key scientific aims of a lander mission to Europa were established and the materials present on the surface of the moon were identified (Hand et al. 2016). Furthermore, information on the anticipated radiation environment was summarised based on the measurements acquired by the Galileo mission during flybys of Europa (Paranicas et al. 2009b). In summary, it was noted that proposed instruments should be designed to survive a proton dose of 150krad.

One example of a material expected to be present on Europa, and that is critical to the mission science goals, is the amino acid alanine, C₃H₇NO₂ (in its various forms). In studies related to the NASA Europa lander call, Wang et al. (2018) recently demonstrated the potential performance of the CIRS instrument in differentiating between the β -, D-, and L- types of alanine (the instrument utilises a CCD47-20, which, in conjunction with the spectrometer optics, exhibits a spectral resolution of 4-6cm⁻¹ (Wang, J. L. Lambert, et al. 2016), see Figure 4.7. The spectrum in Figure 5.31 demonstrates how the dark signal of the CCD47-20 significantly increases after irradiation (to a fluence of 1×10^{11} protons/cm²) and compromises spectral acquisition at warmer (e.g. room) temperatures, to the extent that the sulphur bands are not identified with significant levels of confidence. However, it was demonstrated during the study that operating the detector at 233K resulted in all of the bands being readily identifiable in all of the radiation damaged regions of the detector. It was also noted that radiation induced charge deferral resulted in a reduction in band intensity and poorer spectral resolution (caused by redistribution of the charge, which was originally associated with the Raman band during transfer of the spectral order towards the readout register).

There are a number of methods of mitigating against the effects of radiation damage. These include:

- Operating the camera system at a reduced temperature (e.g. ≤233K) in order to minimise the level of dark signal (although, it should be noted that this can reduce the effects of natural annealing processes);
- Ensuring the number of charge transfers is minimised (i.e. placing the orders as close as possible to the readout register – although, this would probably require the inclusion of an alignment mechanism to adjust for mechanical tolerances that may result in the spectral order missing the detector focal plane);
- Utilising multiple readout registers and (output nodes) to avoid charge deferral contaminating data contained in other spectral orders, see Figure 4.38.

In this chapter, a camera system design is proposed that utilises a number of these mitigation techniques. The CCD230-42, a CCD from e2v-Teledyne, incorporates two readout registers and four output nodes. The image clocks can be sequenced such that each quadrant of the detector is read out through a different corner (output). Consequently, for a Raman spectrometer with two spectral orders it is possible to ensure that the signal from one order does not contaminate the other order (i.e. one order can be transferred to the top readout register and the other order to the bottom readout register, as detailed in Section 4.5). Furthermore, if the optics are configured appropriately, it is possible to arrange for the two spectral orders to be positioned closely to their respective readout register (thereby minimising the impact of charge transfer inefficiencies). To demonstrate the capability of such a system, a prototype Raman spectrometer and camera system were developed in order to verify performance using a number of Europa analogue samples.

During the development of the instrument, a number of studies/trade-offs were performed to determine if it would be possible to utilise the same camera system for additional (complementary) analyses (the size and format of the CCD230-42 effectively enables independent operation of four separate detector regions). This approach significantly decreases the mass, volume, and power budgets associated with developing three (or four) independent instruments. Experience from field studies suggested that the inclusion of a context imager, UV-Vis reflectance imager, and/or XRF/LIBS elemental analyser would significantly enhance scientific return. Consequently, during the development and build of the prototype described in this chapter, the capability of the system to perform a number of different types of analytical measurement were investigated/studied in detail (giving careful consideration to the impact of the challenging radiation environment associated with Europa).

6.1 INSTRUMENT DESIGN

The initial design of the instrument focussed on delivering optimum Raman performance whilst making use of a highly flexible, low mass, and low power approach (e.g. mixed signal CDS ASIC based system) that ensured that the instrument would meet the budget requirements of the Europa lander mission. The requirements for the instrument development include the following functionalities:

- Intelligent pixel/ROI addressing for greater efficiency in data processing and data storage;
- Real time, low level data processing including data compression, transient identification, event identification, and overall autonomous instrument control;
- Acquisition of data at high frame rates in order to satisfy surface measurement requirements, enabling:
 - Provision of greater scientific return in a reduced acquisition period (e.g. a few hours);
 - Mitigation of radiation effects (see Section 4.5 for discussion of readout speed and CTE); and
 - Reduction of instrument noise (such as dark current and ambient light – e.g. performing Raman spectroscopy with a pulsed laser and utilising a shutter/frame transfer mode so that the impact of ambient light is reduced).

In order to fully optimise the performance of the instrument, it was decided to develop a flexible drive and acquisition system that could be interfaced to a number of different detectors (i.e. through the use of interchangeable detector front end modules, that incorporate individual proximity boards for specific detectors types – e.g. CCD47-20, CCD42-10, CCD230-42, CIS120, see Figure 6.1). A common data processor and thermal controller unit was also developed that could be used with any of the detectors. The detector drive system was scoped in order to meet the requirements of the most complex detector types available (and included options for driving detectors with image stores and two, three, or four image clocks). Specifically, the electronics used in the flexible/interchangeable system include:

- Detector headboards with a common system electrical interface (designed with appropriate thermal isolation and local filtering/signal amplification and digitisation);
- Drive system that generates an appropriate number of bias levels for all detectors listed above (i.e. including both CCD and CMOS options);
- Flexible parameter based clock sequencer for complex CCD operating modes;
- A TEC based thermal and cooling temperature stabilisation system (capable of stabilising detector operating temperatures within 0.25K);
- Mechanical shutter control system;
- Laser/diode interface controllers;
- Data processing system used to co-ordinate and combine digitised data from multiple detector outputs that is also capable of performing low level processing algorithms (e.g. data compression);
- Data acquisition system, which consists of appropriate amounts of SDRAM for buffering and frame storage;
- Housekeeping tracking systems (for acquiring and storing instrument health data).



Figure 6.1: the image on the left shows a circuit schematic of the CCD47-20 headboard, pictured on the right with the CCD47-20 integrated.

The CDS ASIC used for noise reduction and digitisation of the CCD signal was the AD9814 (Analogue Devices Inc 1999). The 14-bit analogue to digital converter utilises a 3-channel architecture that has the ability to sample and condition 3 separate channels at a rate of 1MHz. The AD9814 can also be used with a CMOS detector (by disabling the onboard CDS functionality).

The FPGA based drive and acquisition system is programmed with Verilog code and utilises a Gigabit Ethernet interface for 2-way data transfer (achieving high data throughputs). A script based system was developed to enable complex operating modes to be implemented rapidly (i.e. enabling low level operations to be grouped together to perform specific types of windowing, binning, instrument control, and low level data processing).

6.1.1 Optics

A flexible set of optics (incorporating a HoloSpec grating and collimating/focussing lenses) were used to deliver optical spectra to the detector system. Raman emission was generated and collected using a small, optical fibre coupled optical head (utilising a 532nm laser). The system can deliver a laser spot as small as 50 microns to the surface of the sample (larger spot sizes can be achieved by defocussing). The system was designed to enable neon/fluorescence calibration lamps to be interchanged with the optical head so that a broad range of detector characterisation tests could be performed.

6.2 CAMERA SYSTEM CHARACTERISATION

A broad range of detector characterisation facilities were developed in order to fully investigate/optimise performance of the camera system and to perform end to end calibration.

6.2.1 Signal-to-Noise Ratio

To determine the largest SNR (DR) achievable with a specific detector, a white light source is focussed onto a spot on the detector using a set of optics and a pinhole and an image is acquired. The input signal is set to an appropriate level to ensure 80% FWC is achieved in a relatively short integration time. The average pixel intensity within a small ROI (e.g. 10x10 pixels) is compared to the noise level of the system (which is independently determined using a rectangular ROI region on the right hand edge of the device, which only incorporates virtual pixels that represent the electronics noise in the system). The level of dark signal is assessed using an ROI that incorporates pixels from the main imaging area of the device, at least 100 pixels away from the edge of the spot.

Tests are typically performed at 293K, 273K, and 263K environments for UV, optical and IR light (UV and IR light measurements were only made at 293K). Two SNR measurements were made during each test using a number of different integration times (in the range of 1 second to 10 minutes). Where operating temperatures are lower than 290K, the detector is integrated into a vacuum chamber and cooled using a thermoelectric cooler or liquid nitrogen. Detector temperature is continuously monitored using a set of platinum resistance thermometer (PRTs) and a dedicated thermal controller.

At least six images are acquired at each temperature for each light source and the average SNR is determined. A typical set of SNR measurements is provided in Table 6.1. An example CCD image incorporating the light spot on a dark background is provided in Figure 6.2. The dark rectangular regions on either side of the image are the underscan and overscan regions (i.e. shielded and virtual pixels used to determine the electronics noise of the camera).

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Light source	Temperature (K)	Integration time 1 (mins)	SNR1	Integration time 2 (mins)	SNR2
UV	293K	3	115	10	500
	263k	3	145	10	3100
Optical	273K	3	130	10	3016
	293K	3	110	10	506
IR	293K	3	112	10	104

Table 6.1: The results of the SNR calculations for images taken at 263K, 273K and 293K for optical light and 293K for UV and IR light.



Figure 6.2: An example image used to calculate SNR. The focussed spot of UV light is located to the right of the image. The dark sections on either side of the image are the underscan and overscan regions.

6.2.2 Dark Current Stability

The average detector dark current level depends on the specific architecture of the device being tested (e.g. AIMO or NIMO). However, instability in detector operating temperature can result in high levels of noise. Consequently, the temperature stability achieved by the thermal control system is verified using long acquisitions at a number of different temperatures (e.g. 10 minutes to a few hours). An example of the temperature stability achieved by the system over a 10 minute period is provided in Table 6.2. A PRT was used to monitor the temperature of the detector. The stability measurements were made at a number of temperatures in the range 247K to 292K.

Time	Detector	
(Minutes)	temperature using	
	TEC temperature	
	stabilisation (K)	
00:00	290.09	
00:30	290.16	
01:00	290.16	
01:30	290.16	
02:00	290.19	
02:30	290.16	
03:00	290.16	
03:30	290.16	
04:00	290.09	
04:30	290.16	
05:00	290.16	
05:30	290.12	
06:00	290.16	
06:30	290.22	
07:00	290.16	
07:30	290.12	
08:00	290.12	
08:30	290.16	
09:00	290.12	
09:30	290.16	
10:00	290.12	

Table 6.2: An example showing the temperature stability at ambient temperature (290K). Note, $1\Omega \cong 0.25$ K

The curve in Figure 6.3 shows the dark current levels expected at a given temperature, and can be used to determine the variation in dark signal noise as a function of thermal stability. The relationship between dark signal level and temperature for one specific type of detector (i.e. Teledyne-e2v CCD42-10) is given by the following equation:

$$Q = Q_0 1.14 \times 10^6 T^3 e^{-\frac{9080}{T}}$$
 (eq. 6.1),

where Q is the dark current, Q_0 is the dark current at 293K (measured as 50.3 electron/second/pixel), and T is the temperature of the system. The temperature controller and PRT used gave the resistance to 1 Ω resolution, equivalent to 0.25K. Using Equation 6.1, a dark current stability of 0.1 electrons/second/pixel is achievable at 270K. The gradient of the dark current curve is shown in Figure 6.3 and the overall dark current stability is shown in Figure 6.4.



Figure 6.3: Dark signal for a CCD42-10 across the temperature range 251K to 295K.



Figure 6.4: Gradient of the curve in Figure 6.3 showing the dark current stability of the CCD42-10.

6.2.3 PRNU

Pixel response non-uniformity can impact on the accuracy of band ratio analyses. Consequently, it is important to determine an accurate PRNU map so that variations in detection efficiency can be corrected at the pixel level. To characterise the pixel response non-uniformity of the camera system, a number of light sources (Tungsten (optical light), Deuterium (UV light) and IR LED) are used in conjunction with a monochromator, and an integrating sphere to provide uniform illumination at a specific wavelength on the detector.

Typically, 25 images are acquired at each wavelength of interest (with an integration time of 30s). The frames are stacked and the large scale variations in light intensity corrected for, in order to obtain a flat field (an example of the correction profile used at a specific wavelength is shown in Figure 6.5). The standard deviation of the wavelength specific image is then determined in order to assess PRNU (see Table 6.3). This is typically repeated 5 times for each wavelength so that an average PRNU can be calculated (mean PRNU values and standard deviations are provided in the table).



Figure 6.5: An example of a correction profile used to determine PRNU for a 532nm measurement.

In order to determine the large scale variations in the flat field, the CCD images are smoothed by convolving with a top hat filter (sizes typically in the range 11 to 21

pixels). These filtered images are then used to correct the raw data (examples of which are provided in Figure 6.6).



Figure 6.6: Example images acquired at 250nm (top) and 500nm (bottom) filtered with an 11x11 mask (left) and 21x21 mask (right).

Wavelength (nm)	PRNU (%)	Standard deviation
250	1.06	0.01
532	1.24	0.03
650	1.09	0.01
850	2.71	1.3

Table 6.3: Measured PRNU values for a CCD42 at four different wavelengths.

6.2.4 Linearity

The overall linearity of the camera system is a key aspect of system performance since it can have a direct effect on determination of Raman bands ratios (i.e. it affects quantitative analysis). To determine the linearity of the camera system, a 532nm spot is focussed onto the surface of the detector as a sequence of images are being acquired. The detector is used in conjunction with a pre-calibrated power meter (the Newport 1936-R model) to determine the light level reaching each pixel (as illustrated in Figure 6.7). The intensity of the spot is varied to ensure that the full dynamic range of the pixel capacity was measured.



Figure 6.7: Setup used to measure the linearity of a camera system.

Tests are performed for signal inputs in the range 0.012nw - 2nw (which represent 0.1%-80% FWC). A linear fit is performed to the data recorded, as shown in Figure 6.8. The average percentage variation from the linear fit is ~3%.



Figure 6.8: Signal values of a typical CCD acquired from various input intensities, illustrating the linearity of the device.
6.2.5 Spectral Responsivity Knowledge

The spectral responsivity of the device, also referred to as the QE, is the measure of the sensitivity of the detector to specific wavelengths of incoming flux. A detector with a high QE (>80%) for 532nm will acquire more Raman signal and achieve a higher SNR than a detector with a lower QE (<50%) at the same wavelength. To measure the spectral responsivity of a CCD, a light source is used with a monochromator and focussing optics to illuminate a spot on the detector (a Deuterium lamp for UV light, a Tungsten lamp for visible light, and an 850nm LED for IR). The spectral variation of each light source is fully characterised and corrected for using a power meter. The emission profiles (i.e. as a function of wavelength) of each light source are shown in Figures 6.9 (UV light), 6.10 (optical light), and 6.11 (IR light). To avoid absorption (e.g. in the case of the UV source), the glass cover is removed from the detector for all spectral response measurements.

The monochromator is cycled through the wavelength range in steps of 5nm and the light is subsequently partially passed through a beam splitter to the CCD, and partially reflected towards the power meter. Combining these values provides an absolute intensity for each wavelength. CCD images are acquired and an average pixel value determined from a large ROI (e.g. 200x200 pixels) is calculated for each image. The emission curves from the illumination sources are provided for a CCD42 in Figure 6.12.



Figure 6.9: Emission profiles for the UV Deuterium lamp. The plot shows the emission profiles (measured with the power meter) acquired with and without optics. The figure also shows the estimated UV emission derived from passing the raw emission through the optic.



Figure 6.10: The emission curves produced by the tungsten lamp. The plot shows a second emission profile obtained to demonstrate system repeatability (green line).



Figure 6.11: The emission curve acquire from the IR LED using the power meter.



Figure 6.12: The emission curves for the full spectral range.

6.2.6 Polarisation Sensitivity

In applications that utilise polarised light, the polarisation sensitivity of the detector needs to be assessed. In order to measure the sensitivity of the CCD detectors, a

Helium-Neon (HeNe) laser is used to produce a monochromatic source of light. Neutral density filters are used to reduce the intensity of the beam to avoid detector saturation. The light is subsequently split into two paths by a beam splitter: along the path of the laser, the light is directed onto the detector; at 45° to the laser, the light is reflected onto a power meter to measure simultaneous readings and image acquisitions. The light along the normal line of the laser is polarised by a fixed linear polariser (to minimise the polarisation effects on the system optics), and subsequently is directed through a half-wave retarder, and an alignment tool, and directed onto the detector, see Figure 6.13.



Figure 6.13: Setup for the polarisation measurements.

The detector (blue) is placed at angles of 0°, 10° and 20° for the measurements. For each position, an image is acquired and simultaneous power meter readings are acquired. The highest intensity in the image is determined, after applying background subtraction and power meter corrections. Example measurements are shown for the visible and UV light sources in the Figures 6.14 and 6.15.



Figure 6.14: Polarisation data obtained using the HeNe laser (633nm) for the detector at angles 0° (top), 10° (middle) and 20° (bottom). The data is represented with the blue line and squares, the fit represented by the orange curve, and the polarisation component of the fit represented by the purple curve.



Figure 6.15: Polarisation data obtained using the deuterium light source through a monochromator (320 nm) for the detector at angles 0° (top), 10° (middle) and 20° (bottom). The data is represented with the blue line and squares, the fit represented by the orange curve, and the polarisation component of the fit represented by the purple curve. Note that the polarisation component for 10° is very low but is not 0.

The data obtained are Fourier transformed in order to identify key frequency components. The frequency components not associated with the fundamental variations caused by the waveplate (i.e. the polarisation angle) are then truncated.

The equation $polarisation = \frac{max-min}{max+min}$ is applied to the data to determine the polarisation sensitivity of each curve. The values obtained are listed in Table 6.4.

Wavelength (nm)	Detector Angle	Polarisation	Error (%)
	(°)	Sensitivity (%)	
633	0	0.6	0.01
	10	0.3	0.02
	20	2.6	0.04
320	0	0.7	0.01
	10	1.2	0.01
	20	2.4	0.04

 Table 6.4: Summary of polarisation sensitivity for three detector angles in the optical and UV range.

6.2.8 Total Hemispherical Reflectivity Knowledge

A high total hemispherical reflectivity (the ratio of incoming light reflected off the imaging area of the CCD) can result in stray light being reflected into unwanted areas of the instrument (thereby reducing overall detector performance). Therefore, tests are performed on individual detectors/packages to determine the overall reflectivity. To perform these tests, light from the Tungsten lamp is passed through the monochromator and integrating sphere. The beam size at the surface of the detector has a radius of \sim 9.4mm. The light reflected from the detector surface then re-enters the integrating sphere (around the outside of a baffle). Figure 6.16 illustrates the optical setup.

The intensity of the reflected beam is measured using the power meter, which is located at one of the exit ports of the integrated sphere. The reflection intensity is measured 5 times (then averaged) for three different locations on the detector. This sequence is repeated for each input wavelength (e.g. 500nm and 850nm).



Figure 6.16: The setup for the total hemispherical reflectivity measurements, showing the relevant angles including angle of incidence on the detector.

To measure and calibrate the losses in the system, the detector is replaced with a mirror of known reflectivity (typical values for the mirror used in the system are $31.3 \pm 2.3\%$). Results from the mirror reflectivity tests are provided in Table 6.5.

The reflectivity of the detector is determined according to the following equation:

$$n_{detector} = \frac{o_{detector}}{LI_{detector}}$$
 (eq. 6.2),

where *n*_{detector} is the reflectivity of the detector, *O*_{detector} is the measured reflection at the output of the integrating sphere, *I*_{detector} is the intensity of the beam on the input to the integrating sphere (via the tube), and *L* is the loss in the system, which is given by

$$L = \frac{O_{mirror}}{I_{mirror}n_{mirror}} \qquad (eq. 6.3),$$

where O_{mirror} is the measured reflection (in the configuration containing a mirror) at the output of the integrating sphere, I_{mirror} is the intensity of the beam at the input to the integrating sphere (in the configuration including the mirror) and n_{mirror} is the reflectivity of the mirror. Measurements are performed at UV, optical, and IR wavelengths in order to fully characterise the system (representative results are provided in Table 6.5).

Wavelength (nm)	Mirror Reflection Intensities (nW)	Input (nW)	Flux at exit port (nW)	Reflectivity (%)
			1.54±0.31%	67.63±5.24%
250	0.88±0.05%	7.46	1.03±0.80%	65.87±9.57%
			1.00±1.24%	63.98±5.37%
500	0.88±0.05%	3.15	0.87±0.28%	10.99±4.57%
			0.88±0.31%	11.15±4.63%
			0.87±0.38%	11.02±4.58%
850	0.88±0.05%	4.14	0.41±3.27%	40.08±0.57%
			0.50±0.60%	47.99±0.20%
			0.41±1.11%	39.78±0.23%

Table 6.5: Total hemispherical reflectivity results for 250nm, 500nm and 850nm on the imaging part of the detector.

6.3 INSTRUMENT CONFIGURATION

Given a comprehensive knowledge of the performance characteristics of the camera system, it is now possible to fully assess the benefits of specific detector operating modes (in relation to the scientific priorities of the Europa mission). As discussed above, the CCD230-42 based camera system provides a large imaging area that can be divided into four independent quadrants (see detector at the top of Figure 6.17). The mask shown in the photograph of the detector in the bottom of Figure 6.17 shows how the large imaging area can be divided into separate regions that can be used for complementary analytical measurements (e.g. optical spectroscopy, context imaging, and XRF on one detector, see Figures 6.20, 6.21, and 6.22). The selection of the most appropriate format of detector and optimal operating modes depends on a complex trade-off between scientific priorities (dictated by the mission goals). The following sections in this chapter describe one particular combination of measurement techniques that are considered to be highly suitable for a Europa lander mission.



Figure 6.17: Top: CCD230-42, bottom: CCD230-42 with shield.

6.3.1 Detector Characteristics

The CCD230-42 incorporates 2048x2064, 15µm square pixels (2064 pixels in the vertical direction). The typical FWC of each pixel is 150,000 electrons, while the typical dark current level across the 183K to 300K range is shown in Figure 6.18 (the dark current level at 248K is 0.2 electron/pixel/second). For a detector with a midband AR coating, the typical QE at 248K at both 500nm and 650nm is 85%, with a PRNU of 3%. Standard CTE measurements for an unirradiated device are 99.9995% for parallel and serial transfers. A schematic of the typical detector illustrating how the device can be operated with 4 independent imaging areas (the clocking phases in each area labelled A to D) with 4 output sources (labelled OS-E to H) is provided in Figure 6.19.



Figure 6.18: The typical dark current generation for a CCD230-42 across 183K to 300K.

6.3.2 Configuration Modes

As described in Section 4.5, it is possible to significantly mitigate against the effects of radiation damage, such as degraded CTE (e.g. charge deferral caused by radiation induced traps) by carefully configuring the instrument (e.g. by placing the spectral orders close to the readout register, or by independently imaging spectral orders). Figures 6.20 and 6.22 show possible readout modes for the CCD230-42. In Figure 6.20, image (a) illustrates a standard full frame readout mode that would result in the orders being clocked through a large number of rows (potentially as high as \sim 2000) to reach the readout register, likely interacting with a high number of traps resulting in the levels of degradation modelled in Chapter 4. Schematic (b) in Figure 6.20 demonstrates a split full frame readout operation using two outputs. This mode would be beneficial assuming the detector had been aligned so one Raman order was positioned in regions D/C, and the second Raman order was aligned to regions B/A. Schematic (c) in Figure 6.20 demonstrates a four-way output readout mode.



BOTTOM

Figure 6.19: The chip schematic of the CCD230-42 showing the 4 imaging areas and 4 outputs (e2v Technologies 2013).

The various frame readout modes described and illustrated in Figure 6.20 can also be utilised as frame transfer readout modes, see Figure 6.22. The schematic (a) in Figure 6.22 demonstrates how regions A and B can be used as a storage region for data acquired in regions C and D (similarly, the schematics (b) and (c) demonstrate how the image regions located nearest to the readout registers (regions A and D) can be used as storage regions for the data acquired in regions B and C). Aluminium shields can be used to cover the storage regions to avoid light falling on the detector during readout; these shields can also be used to reduce radiation damage, resulting

TOP

in the storage regions being less affected by the radiation damage (and hence reducing the effects of the radiation damage during readout).



Figure 6.20: schematic of the possible full frame readout processes utilising some or all of the image regions and outputs.







Figure 6.22: schematic of the possible frame transfer readout processes utilising some or all of the image regions and outputs.

For the scientific goals of the Europa mission, optimum configurations for the instrument design could be either:

- A camera system with four independent quadrants assigned to Raman spectroscopy, XRF, a context image, and UV fluorescence or UV-Vis reflectance image;
- A detector configuration incorporating Raman orders on two quadrants (top and bottom), and a context image and UV-Vis reflectance image in the other two quadrants.

Due to the instrument accommodation constraints associated with the Europa lander payload, the second configuration is deemed to be the most suitable and measurements performed with such a system are reported in the next section. A detailed schematic of the instrument configuration for this option is provided in Figure 6.21.

6.4 INSTRUMENT PERFORMANCE TESTS RESULTS

The full characterisation of a camera system utilising complementary analytical techniques and multiple outputs was performed using a variety of analogue samples deemed to be representative of Europa material (see Section 4.1.1).

6.4.1 Raman Spectroscopy

Spectra were acquired using the RLS prototype developed by the University of Leicester. The instrument comprises a single mode diode pumped, solid state laser that produces continuous 532nm laser light at a maximum power of 100mW. In conjunction with a MultiRxn Probe optical head, laser light is focused into a 50-100µm spot on the sample surface. Scattered light is collected by the same optic and filtered by a notch filter that reflects light at 532nm with an efficiency of 99%. The prototype system encompasses a HoloSpec, f/1.8 spectrograph. It features an circular entrance slit 100µm in diameter which projects light onto a HoloPlex HPG-532, holographic transmission grating, which disperses the collected 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. A photograph of the spectrograph can be seen in Figure 6.23.



Figure 6.23: Spectograph used in the RLS prototype developed at the University of Leicester.

To demonstrate the capability of the detector and the benefits of quadrant readout, spectral data was acquired using a fluorescent lamp, a source that provided a large

number of strong emission bands (as well as weaker emission bands spanning both orders). The spectrum of the light source can be seen Figure 6.24.



Figure 6.24: Spectrum of the light source (credit: epiphanots).

This study also highlighted the impact of shuttering (either via a mechanical shutter or through frame transfer operation). In this study a mechanical shutter was placed between the CCD detector and the spectrograph exit. The shutter was electrically pulsed by the FPGA camera control system, synchronising the aperture close process with the detector read out sequence.

Figure 6.25 shows a CCD image containing the emission bands from a fluorescence lamp using the prototype instrument described above. The image was acquired using an integration time of 0.1 seconds and a readout frequency of 150kHz.



Figure 6.25: Two Raman orders acquired with the detector and no shutter.



Figure 6.26: Two Raman orders acquired with the use of a shutter.

The introduction of a mechanical shutter and the impact on the resulting CCD image can be seen in Figure 6.26. The image was acquired using an integration time and a shutter open period of 0.1 seconds.

To demonstrate the benefits of using a quadrant device, the spectral orders were shifted into separate quadrants (shown in Figure 6.27).



Figure 6.27: One Raman order on each quadrant acquired using a shutter



Figure 6.28: Raman orders over two quadrants without the use of a shutter.

The orders are clearly in two separately device regions that have been added together after the image has been acquired. Figure 6.28 shows a CCD image with the two orders projected onto the separate quadrants, but without the implementation of a shutter mechanism. The image was acquired by integrating the device for 0.1s and reading the sections out at a frequency of 150Kz.

6.4.2 Context Imaging

Images were acquired using a 2.5cm plano-convex lens. The detector was positioned at 7.5cm from the lens. To demonstrate the imaging capability of the system, various samples and objects, of varying contrast were imaged. Figure 6.29 shows a high contrast image. The image was acquired using an integration time of 0.1s, in a 1x1 binning mode and at a readout speed of 150kHz. A shutter mechanism was used to reduce image smear.



Figure 6.29: High contrast image demonstrating capability of context imager.

The imaging system was also configured to image sample surfaces, similar to those that would be analysed with the Raman or UV-Vis reflectance image. A sample of serpentine was imaged using only a single quadrant of the device. An example image can be seen in Figure 6.30.



Figure 6.30: Serpentine image acquired with context imager.

6.4.3 UV Fluorescence spectroscopy

UV-Vis reflectance imaging was performed using the OMNI- λ 1509 Monochromator, in conjunction with a Xeon arc light source. The monochromator has a wavelength range of 185 nm – far infrared, depending on grating(s) used. The monochromator has a dual grating turret able to house 2 gratings simultaneously. It has an adjustable slit width of 0.01 mm – 3 mm, and a slit height of 4 mm. The slit width is adjusted using the manual precision micrometre. The monochromator has a focal length of 150 mm. An image of the OMNI- λ 1509 Monochromator is shown in Figure 6.31.



Figure 6.31: OMNI-λ 1509 Monochromator used for the UV-Vis reflectance imaging.



Figure 6.32: Emission spectrum of the Xenon arc lamp.

The emission spectrum of the xenon arc lamp can be seen in Figure 6.32. The sample was positioned 15cm from the monochromator exit aperture and was illuminated by the exit beam. A particular UV wavelength was selected by tuning the monochromator and optimising the exit aperture size as to illuminate an area of 1cm^2 section of the sample. The detector was placed at an angle of 45° to the sample surface (to maximise reflection emission), and was coupled with a UV enhanced lens in order to image the illuminated area on the surface sample.

The monochromator was used to shift between wavelengths of 300nm, 400nm and 550nm. At each wavelength, an image was acquired using the CCD. The image integration times were 0.1s throughout the test. Figure 6.33 shows an example CCD image acquired when the sample was illuminated with each wavelength.



Figure 6.33: Example images acquired of samples UV-Vis reflectance imaging.

6.5 DISCUSSION

6.5.1 Raman Spectroscopy

The two diffraction orders produced by the spectrograph are clearly evident in Figures 6.25 and 6.26. The two orders are sufficiently intense that during the readout process, the light that continues to fall on the detector can be seen over the entire device. This has led to order contamination, i.e. light usually confined to one of the diffraction orders is contaminating with the other order transferring unwanted signal to a different part of the spectrum.

However, Figure 6.26 shows the same two diffraction orders acquired with the use of a shutter, with no observable image smear. Mechanical shutters are rarely used in space applications as the mechanism is unreliable. A potential mitigation process is to use a frame transfer device as discussed in Section 6.3. However, to combine analytical techniques and reduce the complexity of the readout sequence a quadrant device was implemented.

Figure 6.27 shows a CCD image with two readout regions (regions on the device that are readout in opposite directions, as illustrated by Figure 6.20). The figure shows an example of a CCD image acquired with a shutter mechanism resulting in a minimal amount of image smear. The subsequent removal of the shutter mechanism produces the amount of image smear observed in Figure 6.28. However, the smear only extends to the edge of the read out region of that particular order and does not reach the other order. This removes need for a shutter mechanism and reduces the chance of order contamination which can lead to ambiguous band identification. The technique also allows for the combination of analytical techniques.

6.5.2 Context imaging

Figures 6.29 and 6.30 show a CCD image containing a close up image of an object at a distance of 30cm from the camera lens. The images demonstrate the detectors ability to image a large region of a sample surface (highlights the contrasting material within the sample) on one quadrant of the device. The CCD system was capable of imaging a 3cm² section of a sample. However, when combined with a

Raman instrument (as the systems context imager) the region in focus would be aligned with the laser focal point, providing a focused context image of the sample surface under analytical investigation, providing visible scientific context to the sample analysis.

6.5.3 UV-Vis Reflectance Imaging

Figure 6.33 shows three images of a serpentine sample obtained following illumination with the UV fluorescence OMNI- λ 1509 Monochromator. Each image was acquired using a different wavelength to illuminate the sample. It is evident that the fluorescence emission from the sample varies depending on the incident wavelength, with 400nm inducing the most intense emission, however all three images demonstrate the CCD systems ability to detect and image varying levels of fluorescence over a sample surface. Figure 6.33 presents a CCD image acquired while using a standard glass cover.

Conclusions and Future Work

The work in this thesis focussed on the optimisation and development of a camera system that can be used as a combined instrument for a mission to Europa. One of the moons of Jupiter, Europa is a key location for the search for life. As summarised in chapter 2, Raman spectroscopy is an ideal analytical technique for analysing materials on the surface of Europa that could address the science goal of searching for life, as well as assessing the habitability of the moon. It is also invaluable to provide complementary data to the molecular information provided by Raman spectroscopy with, for example, UV-Vis reflectance imaging and/or XRF, also described in chapter 2.

Modern technology and advancements in the design and development of the solid state detectors usable for an instrument to Europa were detailed in chapter 3. The performance characteristics and design types of two possible detectors (the CCD and CMOS devices) were described in terms of their performance under hostile environments (that are present on Europa).

In chapter 4, a Monte Carlo model was developed to simulate the effects of a high radiation environment on the devices outlined in chapter 3, with specific focus on their performance as a Raman spectrometer detector. The dark signal levels were determined to significantly increase in a CCD under high fluence levels, significantly reducing the SNR and dynamic range of the detector. Notably, the dark signal levels in the CMOS device were not as affected under the same fluence levels. Furthermore, additional mitigation strategies were also investigated to verify the effects of radiation transfer on charge transfer efficiency. In addition, camera system configurations were proposed that ensured the performance of the system was maximised following significant levels of radiation.

A representative detector (that has been integrated into a Raman spectrometer for proposals to missions to Mars and the Moon) was subjected to irradiation at a range of fluence levels to monitor the degradation in performance. The measurements made on the dark signal levels confirmed the significant increase predicted after irradiation of high proton fluence levels. However, it was determined that operating at lower temperatures (such as 233K and lower) greatly decreased the dark signal

level, resulting in a performance of the detector similar to a non-radiation damaged device.

In chapter 6, a full camera system design was described that could utilise some of the high radiation mitigation techniques, such as a multi-readout register device. A summary of performance and characterisation tests was outlined for a suitably representative detector. Furthermore, a possible flight detector (CCD) with an appropriately manufactured mask was integrated into the system to demonstrate the performance of a combined analytical instrument (by performing Raman spectroscopy, context imaging, and UV-Vis reflectance imaging) that utilises a signal detector system (significantly saving on mass, thermal, volume and data processing budgets). This combined instrument will be further developed and optimised to provide optimal scientific return for a Europa mission whilst operating under the high radiation environment.

FUTURE WORK

Future work will include using the model to simulate the effects of radiation damage in the CMOS devices to provide a comparison with the expected degradation in performance in the CCD. Furthermore, future radiation campaigns will be performed on more devices, including CMOS detectors and other types of CCD (e.g. nitride thinned detectors). All detectors will be irradiated with similar fluences to those expected at Europa, and the ability of the camera system to acquire data with the required performance features (e.g. SNR, DR) will be assessed (i.e. the software model and radiation data will enable detailed but fast trade-offs to be performed).

All devices will be used to analyse a wider range of Europa analogue samples, to provide a more in depth assessment of detector performance in terms of addressing the science goals of a Europa mission. Work will focus on developing an optimal combined instrument by assessing which complementary techniques provide the greatest scientific return and can reduce mass, volume, and power budgets.

Once the optimal solid state detector (for operating under hostile environments) has been chosen and appropriate operating modes (e.g. multi readout register transfers) have been optimised, the combined instrument will undergo a full range of environmental tests to improve the TRL (e.g. shock, vibration, and thermal tests).

The system will then be utilised by NASA partners (JPL) to perform tests with flight representative optics in the laboratory and in the field.

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