Terahertz Technology and Applications: 3D Printing and Art Conservation

Andrew Donald Squires

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Terahertz Technology and Applications: 3D Printing and Art Conservation

Andrew Donald Squires

Supervisor:
Prof. R. A. Lewis

This thesis is presented as part of the requirements for the conferral of the degree:

Doctor of Philosophy

The University of Wollongong
School of Physics

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Declaration

I, Andrew Donald Squires, declare that this thesis submitted in partial fulfilment of the requirements for the conferral of the degree Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Andrew Donald Squires
November 20, 2017
Abstract

Terahertz methods have developed strongly in recent years resulting in an emergence of applications spanning many research fields. This is owing to desirable properties of the terahertz wave; large penetration depths in dielectric materials with non-ionisation, coupled with the origin of many physical phenomena, like vibrational modes, occurring at terahertz frequencies. This thesis explores these advantages in two contemporary research areas; 3D printing and art conservation science.

3D printing is shown to be a desirable modality to couple with terahertz techniques with printable dielectric materials allowing for rapid, customisable terahertz components, even with the cheapest and simplest form, fused filament fabrication. Specifically, commercial filament materials are characterised and evaluated in the terahertz regime in conjunction to producing functional components, namely diffractive optics and a hyperuniform waveguide.

Terahertz applications in art conservation science are investigated through critical analysis of a series of synthetic and natural pigments. Quinacridone and phthalocyanine, the most important synthetic pigments in red-violet and blue-green shades respectively are shown to have ‘fingerprint’ spectra, with associated temperature dependence. Terahertz photons distinguish polymorphs of these pigments, not achievable with competing modalities using x-rays. Earth-based iron oxide pigments found in many indigenous and culturally significant artefacts also show characteristic, sometimes temperature dependent, absorptions for terahertz frequencies. Strong distinction is shown for natural and synthetic counterparts of the same pigment class with subtle variations in similar pigments from varying geographical origins. Terahertz spectroscopy confirms utility in this research field in identifying optically similar materials, fraud detection in reproductions, dating of artworks and sourcing the geographical origin of culturally significant items.
Publications

Much of the work presented in this thesis has been published in peer reviewed journals or presented at conferences. These are listed below.

**Journal Articles**


**Conference Proceedings**


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Chapter 1

Introduction

The work embodied in this thesis aims to critically analyse and evaluate the utility of terahertz techniques in two contemporary research fields: 3D printing and art conservation science. Chapter 2 sets the scene with a relevant review of the literature, focused on the scientific methods and research pertinent to the experimentation carried out in this work. A further layer of depth is introduced in chapter 3. This chapter expands on the fundamental principles presented in the literature review related to the experimental techniques necessary in investigating 3D printed materials and art pigmentations. Chapter 4 looks at the relationship between terahertz systems and 3D printing while chapter 5 analyses the terahertz response of a series of pigments relevant to contemporary and historic artefacts. Chapter 6 summarises the main experimental results presented throughout this thesis.

Terahertz spectroscopy has a mutualistic relationship with recent advancements in 3D printing technology. The terahertz field stands to gain from the rapid, cheap and customisable devices 3D printing offers, while additive manufacturing gains from the material insight available from terahertz waves. These are both explored in this thesis. Material characterisation is performed via time domain spectroscopy on the full array of commercial printer filaments, in conjunction with assessment on their mechanical properties and overall printability. Many filaments are modified in search of desirable mechanical traits or visual appeal. The terahertz response of these are of particular interest. Dielectric optical devices are hence designed, printed and tested, increasing in their complexity from simple diffractive optics to a hyperuniform waveguide. This adds scope and insight into the feasibility of 3D printing in the terahertz regime and identifies superior materials in printing lab based optical components.

A new, exciting field recently acquiring terahertz applications is conservation science. New improved sources and detection methods have spearheaded the viability of portable systems, which can non destructively and non invasively inspect items of cultural significance. This is highly desirable to any conservator. With such
a large array of materials used in contemporary artworks and across the centuries, a correspondingly vast database, and understanding of the terahertz response to these materials, is required. This is currently lacking, reducing many studies to giving phenomenological results. Research presented in chapter 5 addresses this issue, specifically in paint pigments. Contemporary synthetic pigments, quinacridone and phthalocyanine alongside their historic natural earth counterparts, iron oxide ochres, are investigated over a large spectral range. Fourier transform and time domain spectroscopy, alongside density functional theory, will provide a sound basis to identifying pigments as well as ascribing physical origins to observed resonances. Measurements are shown from room temperature down to 10 K revealing compelling temperature dynamics.
Chapter 2

Literature Review

This chapter will provide a critical review of the relevant research pertaining to experimental work presented in this thesis. Overviews of the relevant fields will be presented, with detailed analysis reserved for items directly applicable to this thesis. Review and analysis of research regarding the apparatus’ function and techniques in spectral analysis is presented in chapter 3.

2.1 Terahertz Radiation

Nestled at the limits of electronic and photonic regions of the electromagnetic spectrum (Fig. 2.1) lies the fabled terahertz (THz) ‘gap.’ Aptly named, applications in this region have typically lagged behind other regions of the electromagnetic spectrum due to limited available source power and sensitive detection methods. Generally, the THz region is defined as between 0.1–10 THz [2], with restrictions in the progress of this region having only been lifted in the last three decades [3]. Recent advances have coincided with large interest and excitement in fundamental research and applications owing to desirable characteristics of the THz wave. THz waves exhibit large penetration depths in dielectric materials such as wood, plastics, paint and paper. The low THz photon energy, \( \sim 4 \text{ meV} \) at 1 THz, coincides with intermolecular vibrations present in chemicals and organic molecules [4]. THz is non-ionising and is a large component of the 10–15 K cosmic background radiation.
Technologies utilising THz radiation began in the 1980’s with techniques in optical rectification and photoconduction advancing sufficiently to allow direct THz production using multi-mode lasers, such as the Ti:Sapphire laser and free electron lasers [5]. In turn, THz optoelectronics emerged as a research field culminating in the first THz-Time Domain Spectrometer (THz-TDS), produced by Grischowsky et al. in 1989 [6, 7] in conjunction with the first spectroscopic measurements of water vapour [8]. This work laid the bedrock for modern day studies in THz physics. Research in this field has since exploded with a recent study showing publication outputs containing ‘terahertz’ in the abstract, title or keyword fields to double approximately every three years [9].

Resulting from this exponential increase in research output with ever improving generation and detection methods, is a wide array of current applications using THz photons. To name a few, THz used in art conservation science [10], medical research [11], identifying explosives and drugs [12], geology [13], wireless communications [14], astronomy [15] and security [16]. This is but a snapshot of the overall impact THz
photons are having in research and industry, which will only improve into the future.

2.2 Terahertz Sources

2.2.1 Thermal Sources

Perhaps the simplest of THz sources are blackbodies emitting in accordance with Planck’s radiation law. Cold stellar bodies and the cosmic background radiate largely in the THz [4]. Approximately half of the total luminosity and 98% of the photons emitted since the Big Bang fall into the microwave and far infrared regions of the electromagnetic spectrum [17]. Large atmospheric absorption, owing to strong rotational modes of water vapour [18] stifles detection and use of this radiation in ground based systems. Typical laboratory thermal sources are the globar [19] and mercury lamp [20]. Globars are typically a rod of silicon carborundum (SiC) operating at temperatures near 1650 K, with an emissivity ranging from 0.5–0.8 [9, 21].

2.2.2 Laser Sources

Laser methods are multi-faceted and widespread as a means of THz production. On one hand, radiation can be produced directly via gas, semiconductor and quantum cascade lasers. On the other, optically pumping devices with visible and infra-red lasers is commonly employed as a method of THz generation. In these applications both continuous and pulsed laser systems are used, dependent on the physical properties of the pumped device.

Gas Lasers

THz generation in gas lasers follows from typical stimulated emission laser techniques. Population inversion is achieved via a CO$_2$ laser. The gain medium comprises molecular gases typically CH$_3$OH, NH$_3$, CH$_2$F$_2$ and CH$_3$F [22]. Permanent dipole moments in these molecules permit direct coupling of the electromagnetic
field to their rotational energies. A population inversion is thus achieved in the rotational energy modes. Subsequent de-excitation results in discrete, high power THz outputs, dependent on the gain medium used. A list of THz gas laser lines is shown in Table 2.1, as presented in [22].

Table 2.1: Laser lines of optically pumped THz gas lasers.

<table>
<thead>
<tr>
<th>Frequency (THz)</th>
<th>Molecule</th>
<th>Output Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>CH$_3$OH</td>
<td>~ 10</td>
</tr>
<tr>
<td>7.1</td>
<td>CH$_3$OH</td>
<td>~ 10</td>
</tr>
<tr>
<td>4.68</td>
<td>CH$_3$OH</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>4.25</td>
<td>CH$_3$OH</td>
<td>~ 100</td>
</tr>
<tr>
<td>3.68</td>
<td>NH$_3$</td>
<td>~ 100</td>
</tr>
<tr>
<td>2.52</td>
<td>CH$_3$OH</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>2.46</td>
<td>CH$_2$F$_2$</td>
<td>~ 10</td>
</tr>
<tr>
<td>1.96</td>
<td>NH$_3$</td>
<td>~ 200</td>
</tr>
<tr>
<td>1.81</td>
<td>CH$_2$F$_2$</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>1.27</td>
<td>CH$_2$F$_2$</td>
<td>~ 10</td>
</tr>
<tr>
<td>0.86</td>
<td>CH$_3$Cl</td>
<td>~ 10</td>
</tr>
<tr>
<td>0.59</td>
<td>CH$_3$I</td>
<td>~ 10</td>
</tr>
<tr>
<td>0.525</td>
<td>CH$_3$OH</td>
<td>~ 40</td>
</tr>
<tr>
<td>0.245</td>
<td>CH$_3$OH</td>
<td>~ 10</td>
</tr>
</tbody>
</table>

Quantum Cascade Lasers

The first THz quantum cascade lasers (QCL’s) were reported in 2002 [24]. In QCL’s, light is produced via intersubband transitions along a series of quantum wells grown from micro-beam epitaxy in III-V semiconductor compounds [25]. Unlike standard semiconductor laser diodes relying on electron-hole recombination, QCL’s utilise a unipolar process, i.e. the intersubband transition only involves electrons. Electrons undergoing the intersubband transition in one quantum well subsequently are injected into the next quantum well, with the process repeating along the entire structure, hence cascading [22]. For THz-QCL’s, a gallium arsenide (GaAs) heterostructure is typically used allowing both continuous wave and pulsed modes of operation [26]. To date, THz-QCL sources can produce power outputs from milliwatts [27] to above tens of milliwatts [25, 26, 28]. The main issues in using THz-
QCL’s are twofold: (1) The low photon energy of the THz radiation implies that typically cryogenic temperatures are required for operation, as thermal vibrations can easily disturb the population inversion required for lasing. (2) The long wavelength of the THz wave poses problems in mode confinement. Metal waveguides are required for confinement despite their high loss [22]. Dielectric waveguides are unsuitable as the evanescent wave is larger than the quantum well structure present in the QCL [22].

2.2.3 Laser Pumped Sources

Laser pumped THz sources fall into two main categories: continuous and pulsed. Pertinent to this thesis, photomixers, typically low temperature grown GaAs [29] are able to cost-effectively produce continuous wave radiation up to 5 THz. The photomixing device is pumped with two near frequency infrared lasers with the output corresponding to the beat frequency. Tuning the pump lasers translates to a continuous tuneable THz source. This is discussed in detail in section 3.3, with this device essential in two colour wave spectroscopy. Green lasers have also been demonstrated to produce THz radiation via mechanical resonances [30].

Pulsed laser sources generate THz radiation via an intrinsic optoelectrical response of the desired material. These include photoconductive switches, where laser pulses briefly close an electrical connection with the geometry determining the THz output. This is the only pulsed laser source relevant to this thesis and will be explained in detail in section 3.1. Frequency mixing via optical rectification and transient currents are other common THz sources utilising femtosecond pulsed lasers [9].

2.2.4 Synchrotron Source

Synchrotrons provide a high power source of THz radiation, based on the principle that accelerating electrons will produce electromagnetic radiation first proposed by Joseph Larmor in the early 1900’s [31]. In a synchrotron, electrons are first acceler-
ated to very high velocity in a linear accelerator before being injected into a booster ring. In this booster ring, synchronised electric and magnetic fields increase the electron velocity to near light speed [32]. At this point the electrons are injected into, and orbit around, a storage ring. The storage consists of many dipole electromagnets used to bend the electrons around the storage ring. In doing so the directional change induces an acceleration, producing electromagnetic radiation. Due to the highly relativistic speeds of the electrons, emitted radiation is compressed into very small, intense pockets of information [33], similar to a sonic boom in sound waves. These intense pockets deliver broadband radiation extending from THz frequencies to hard x-rays [34]. Beamlines are situated around the storage ring each with its own desired equipment, spectroscopy and detection setups. The consequential THz output is highly brilliant, hundreds of thousands times more intense than a globar source [35]. State-of-the-art optics coupled to this high brilliance source at the Australian Synchrotron gives a 400 µm point size, with incredibly high flux density well suited for small samples with high transmissive losses.

2.2.5 Other Terahertz Sources

Other common THz sources not relevant to the experimental work partaken in this thesis include mercury lamps [20], backward wave oscillators [36, 37], gyrotrons [38], free electron lasers [39], Josephson junctions in superconductors and even peeling sticky tape [40]. These are categorised, nicely detailed and explored by Lewis in [9].

2.3 Terahertz Detectors

Terahertz detection is subject to many of the same issues outlined previously in generating and using THz radiation. Low THz source power and short propagation lengths in free space require advanced and sensitive detection methods. Loosely speaking, we can categorise the detectors into those that only measure THz amplitude (incoherent) and those which can measure amplitude and phase (coherent).
CHAPTER 2. LITERATURE REVIEW

The semiconductor bolometer, is an incoherent detector and is the most frequently used in data taking throughout this thesis. This consists of a heavily doped semiconductor, typically silicon, which conducts via a hopping process leading to a resistivity proportional to \(\exp(T/T_0)\) \([41]\). Thermal (THz) radiation incident on the semiconductor increases the resistance measured externally as a voltage signal. This can detect incident power of \(10^{-13}\) W \([42]\), with a responsivity of the order of \(10^8\) V/W and a noise equivalent power of \(10^{-17}\) W/\(\sqrt{\text{Hz}}\) \([41]\). One drawback with the bolometer is the effects of thermal noise. Minimising this requires cryogenic operation, with liquid helium at 4 K in an inner chamber in thermal contact with the resistive element. Further preparation is required in evacuating the outer regions of the detector reducing heat transfer causing boil-off of the helium. Older bolometers give around 12 hrs of useable operation before warming up, with newer devices extending this into the region of 30 hrs.

Room temperature incoherent detectors include the Golay cell and other pyroelectric detectors. In the Golay cell a small gaseous volume contained in a membrane is heated thermally, expanding the membrane. This mechanical change is measured. Generally, the Golay cell and pyroelectric detectors give a noise equivalent power of \(10^{-9}\) W/\(\sqrt{\text{Hz}}\) \([41]\). Despite room temperature operation, Golay cells are very slow as thermal equilibrium must be reached before a measurement is taken. They require a low frequency modulation of the source below 20 Hz.

Coherent detectors are based on the optoelectrical properties of, for example, birefringent crystals and photoconductive switches. In the former, electro-optic sampling (EOS) exploits the linear electro-optic (Pockel) effect, where propagation of the optical probe is modulated by the THz electric field over a short timescale. This produces a change in polarisation, which with a complex of polarisers, can be measured as a change in optical power \([5]\). In photoconductive switches the probe optical pulse closes an electrical connection in the photoconductive device for a short time. A THz pulse produces a bias electric field across the device and subsequently induces a photocurrent which is measured externally \([5]\). These methods are widely
used in TDS systems. They typically form part of a proprietary spectroscopy system and thus can not be easily manipulated, unlike the incoherent detectors, transported at will around the lab. Details of the detection methods in the TDS systems is illustrated in section 3.1.

2.4 Terahertz and 3-Dimensional Printing

Recent years have seen additive manufacturing (3D printing) revolutionise many aspects of the manufacturing industry, allowing cheap, rapid and customisable fabrication of elements to be used functionally or in prototyping. In 3D printing, items are generated via additive methods, which sees final products built up a single layer at a time from the ground up. This is in direct contrast to other subtractive methods, where material is removed from bulk via, for example, milling on a CNC machine or turning on a lathe.

Additive manufacturing concepts have been applied in multitudes of ways, leading to a wide array of 3D printing technologies [43]. In turn, this allows 3D printing across many materials and applications. The most common and leading technologies in 3D printing include: Fused Deposition Modelling (FDM) also called Fused Filament Fabrication (FFF), Stereolithography (SLA), Digital Light Processing (DLP), Selective Laser Sintering (SLS), Inkjet Printing, Selective Laser Melting (SLM) and Electron Beam Melting (EBM) [44, 45].

![Figure 2.2: Schematic of the 3D printing process.](image)

Fig. 2.2 shows the 3D printing process. A desired model is designed, typically in CAD, before being exported into proprietary software which interfaces with a 3D printer. This software ‘slices’ the 3D model along the Z axis at intervals preset by the
user within physical limitations of the printer. Each model ‘slice’ is converted into G-code and sent sequentially to a 3D printer which builds the model one layer at a time. When finished, the final model is generally ‘post-processed’, removing model supports, sanding and possibly painting/sealing the final part. This process has distinct advantages over subtractive methods, allowing production of devices with internal structures and previously unavailable geometries, like parabolic designs, with minimum waste material.

The most common and cost effective form of 3D printing is Fused Deposition Modelling (FDM), developed by Stratasys [46]. In FDM, shown in Fig. 2.3, a thermoplastic polymer is extruded onto a print bed, following the generated paths in a sliced model’s G-code. The polymer material is pulled from a spool by a drive gear into a hot-end. This consists of a heater block in thermodynamic equilibrium with the extruder nozzle. The plastic is melted in this section with pressure from the drive gear ensuring material is extruded onto the print bed. In some cases this print bed may be heated. The temperatures of the hot end are generally in the order of $200\,\degree C$, with print bed temperatures ranging from room temperature to $130\,\degree C$. The exact temperatures needed depend on the polymer thermal properties, specifically the glass transition temperature and coefficient of thermal expansion. The most common plastics used with this technology are Acrylonitrile Butadiene Styrene (ABS) and Polylactic Acid (PLA) [46]. These provide the most cost-effective and easy to use form of 3D printing [45]. Recently, engineered variants of these polymers have become available, as well as many other exotic filaments including: nylon, polypropylene, polycarbonate, polyethylene terephthalate and metallic blends consisting of copper, brass, bronze, tungsten and bismuth.

In FDM the absolute resolution limit of the printer is bound by the diameter of the extrusion nozzle, typically 0.4 mm. While adequate for the hobbyist, the engineer would prefer much higher precision. One such system, explored in this thesis, is inkjet 3D printing technology also referred to as Multijet (MJT) and Polyjet (PJT) printing. This is a subset of the photopolymerisation method, where a liquid
photopolymer is selectively cured by light-activated polymerisation [44] Shown in Fig. 2.4, this method prints using a photocurable resin [47]. This is laid very finely from a series of inkjet printheads, which jet droplets of resin with high precision, subsequently cured with a flash from a UV lamp. This system lowers the minimum layer height from 100 µm in FDM to 15 µm [45]. Further the thinnest stand alone structure is reduced from 400 µm to around 200 µm.

THz methods stand to benefit substantially from this technology. Typical THz optics consist of diffraction gratings, lenses [48] waveguides/ dielectric fibers [49] and prisms [50]. Conventionally, optical elements have been made by subtractive methods, such as machining lenses on a lathe [51], or cutting grooves in a substrate to form a diffraction grating [52, 53].

3D printed THz devices have rapidly developed over recent years [54]. This is
especially apparent in passive dielectric devices. Diffraction gratings [55] have been demonstrated, as have a range of lenses [56, 57]. In these devices, bulk absorption in the thermoplastic used leads to high absorption losses. As such, hyperbolic fresnel lenses tailor made for THz linear scanners [58] and metasurface flat lens arrays [59] have been developed, emphasising the advantages of rapid, customiseable prototyping evident in 3D printing THz optics. A range of 3D printed waveguides and antennas [60] have emerged; Plasmonic guides for surface plasma polariton propagation [61] as well as photonic crystal waveguides with periodic triangular structures surrounding an air core [62]. Similarly hyperuniform waveguides with periodic disordered reflectors surrounding an air core [63] have resulted measured photonic band gaps. Other examples of hollow core waveguides with periodic cladding structure are given in [64]. A 3D printed anti-reflection waveguide structure has shown low loss, close to zero dispersion of THz waves [65]. In a slightly more exotic case, guide cladding is customised by 3D printing to contain metal inclusions inserted post production [66]. Rapid prototyping has proved fruitful in testing periodic designs for use in a two-dimensional periodic surface lattice required in electron beam guidance [67]. Further electromagnetic bandgap structures [68] have been realised as have dielectric metamaterials [69]. With the advent of metallicised 3D printer filament, a recent work has even developed 3D printed metallic rectangular waveguides [70]. Quasi-Wollaston prisms [71] were printed recently.

The vast majority of the cited research occurs within the last three years, evident of the current high interest in 3D printing THz devices. With such a large array of printable materials available, even in entry level research printers, systematic broadband characterisation becomes desirable. This is particularly warranted with many proprietary materials containing in house modifications, which in some cases, drastically alter the THz response, despite remaining unchanged to visible photons. These modifications are aimed at enhancing optical (visible), mechanical and printability properties of the thermoplastic material.
CHAPTER 2. LITERATURE REVIEW

2.5 Terahertz and Art Conservation Science

Recent years have seen a large development in the use of THz radiation for applications in art analysis and conservation science. Reasons for this are two-fold. (1) Favourable characteristics of THz allow a large depth penetration into dielectric materials permitting *in situ*, non-destructive and non-invasive analysis of artworks and culturally significant pieces, along with their constituent surface and sub-surface (Fig. 2.5) materials [72, 73], including pigments, binders and substrates [74, 75]. THz photons show large penetration depths as dielectric constants are inversely proportional to frequency. Thus, as frequencies are increased into infrared and visible photons, dielectrics will become more highly absorbing. Furthermore, these materials exhibit a large number of molecular resonances in the far to mid infrared regions extending into atomic transitions as visible photons are approached. This serves only to further increase absorbance in these regions. X-rays exceed THz penetration depths, owing to their very high photon energies. (2) Developments in THz technologies have given rise to more powerful sources and sensitive detection methods to the point of portable devices currently being commercially available [76], used not just in art conservation but also non-destructive testing in industry [77].

The amalgamation of these two points has lead to widespread applications of THz techniques in this research field. Fukunaga and Picollo [73] review and show the utility of THz spectroscopy in identifying many pigments, binders and substrates, in both transmission and reflection geometries. Further, it is demonstrated that various combinations of the materials can be identified, as mixing of the pigments, glues and binders does not introduce chemical changes to each individual material. The dielectric properties of polymers are revealed in THz spectroscopy [78], which in turn has seen applications of THz spectroscopy in the investigation of historic plastics and polymers [79].

These characteristics, with depth penetration have led to sub-surface THz imaging of many intriguing items. In [80] items from the Tokyo National Museum and Museum of Aquitaine (France) have been imaged, namely a Japanese panel screen,
African fetish figures and a 3500 yr old Egyptian jar. Most notably, THz imaging revealed, non invasively, internal bodies in the African figure and Egyptian Jar, later confirmed to be a snake head (Fig. 2.6) and grains when investigated with x-ray radiography. This is a good illustration of the real-world application of THz imaging, seen as a first point of call and complementary technique to x-rays and neutron scattering. THz imaging techniques reveal items of interest but often lack the high resolution required due to the larger wavelengths involved. Thus these images provide identification and justification for further, extensive studies.

THz imaging has recently been found to be extremely useful in investigating panel paintings with many closely spaced layers [81]. Reflection spectra have permitted simultaneous sub-surface imaging of all the paint and preparation layers revealing key new insights. In [82] two stratigraphic tempera panel paintings are investigated, the Badia by Giotto di Bondone (1300) and the San Giovenale by Masaccio (1422). In the former, as shown in Fig. 2.7, preparatory layers were shown to be lost under a crack, with repairs only extending to the surface paint layer. In the latter, a section burnt by candle wax was revealed to have subsequent damage.
extending to the wood substrate, beyond the paint, preparation and canvas layers. This type of information is vital to conservators. This imaging technique has also been applied to panel paintings beneath gilded finishes [83], mural paintings [84] and wooden panel paintings [85].

Further extension of THz techniques in more exotic conservation sciences have also seen utility in reproducing internal structures of stone sculptures [86] as well as wall plaster in culturally important buildings across Europe [87].

Despite the rapid growth of research utilising THz techniques in art conservation science, studies are generally phenomenological. Even literature giving characteristic spectral features fail to give physical origin of the observed resonances. A comprehensive database of materials, with identifying physical information is currently lacking in this research field [72, 88]. Addressing, in part, this issue is a goal of this thesis and current research.
Figure 2.7: St. Benedict in Badia with THz techniques detailing sub-surface preparation layers lost due to a crack. Taken from [82].
Chapter 3

Experimental Methods

This chapter will elaborate on the theory presented in the literature review and discuss its direct application in a series of experimental setups used throughout the experimental chapters of this thesis. Discussion of the theory in each case is kept within relevance to experimental procedures used throughout later chapters. The TDS systems presented in sections 3.1.1 and 3.1.2 were used in both experimental chapters, particularly in optical characterisation of the 3D printer plastics in Chapter 4 and lower frequency regions of quinacridone and phthalocyanine pigments in Chapter 5. The FTIR system in section 3.2 is used in the higher frequency measurements of the quinacridone and phthalocyanine pigments, while the Bruker system at the Australian synchrotron was used for all temperature dependence measurements presented in Chapter 5. Section 3.3 shows a Two Colour system. This was used predominately in characterising 3D printed diffraction grating and lenses in Chapter 4.3. Finally, powder x-ray diffraction explained in 3.4 was utilised in verifying the composition of the quinacridone and phthalocyanine pigments in Chapter 5.

3.1 Terahertz Time Domain Spectroscopy

A schematic of a simple THz-TDS system is shown in Fig. 3.1. A mode-locked, typically Ti: sapphire laser produces around 800nm pulses with a time width <100 fs [89]. Beamsplitting separates the laser source into ‘pump’ and ‘probe’ beams. The
Figure 3.1: Schematic of terahertz time domain system. Optics included to focus the beam at the sample position are omitted for clarity.

The pump beam falls incident on a THz emitter, typically a birefringent crystal [90, 91] or photoconductive switch [92], creating a transient THz pulse, approximately 1 ps, in free space. The probe beam, coupled to a fast electrical detector is used to gate the THz pulse. An optical delay, usually a mechanical stage, alters the phase between the THz transient and probe pulse incident on the detector. With a detector response proportional to the THz electric field, small adjustments of the optical delay allow probing of the full THz pulse, subsequently producing a time-dependent signal of the THz electric field [92] (Fig. 3.2).

The use of coherent pulses in THz-TDS gives distinct advantages over FTIR methods [93]. The pump-probe system allows simultaneous measurement of the THz electric field amplitude and phase, circumventing the need to use Kramers-Kronig transformations [89].

Without the need for Kramers-Kronig transformations, real and imaginary terms of optical parameters can be obtained concurrently with Fourier analysis of the time domain waveforms. Sample analysis is made by comparing the electric field of two waveforms, one with a sample of interest, $E_{\text{Sample}}(t)$, and a reference without
the sample, $E_{\text{Reference}}(t)$. By taking Fourier transforms the corresponding complex amplitudes $E_{\text{Sample}}(\omega)$ and $E_{\text{Reference}}(\omega)$ are obtained [26]:

$$
E(\omega) = A(\omega)e^{-i\phi(\omega)} = \int_{-\infty}^{\infty} E(t)e^{-i\omega t} dt
$$

(3.1)

If a dielectric material of thickness, $d$, is placed at normal incidence to the THz beam, assuming no internal reflections, the electric field through the sample can be expressed as: [94]

$$
E_{\text{Sample}} = \eta \cdot \frac{4\tilde{n}_s(\omega)}{\tilde{n}_s(\omega) + 1} \cdot e^{-i\tilde{n}_s(\omega) \frac{\omega d}{c}} \cdot E_0(\omega)
$$

(3.2)

With a corresponding reference $E$ field with no dielectric sample:

$$
E_{\text{Reference}} = \eta \cdot e^{i\omega d} \cdot E_0(\omega)
$$

(3.3)

Here, $\eta$ refers to the free space transmission factor with the dielectric complex refractive index $\tilde{n}_s(\omega)$ more accurately given by:

$$
\tilde{n}_s(\omega) = n_s(\omega) + i\kappa_s(\omega)
$$

(3.4)
CHAPTER 3. EXPERIMENTAL METHODS

Where \( n_s(\omega) \) refers to the real refractive index and \( \kappa_s(\omega) \) is the extinction coefficient. Taking the ratio of equation 3.2 with 3.3 gives the complex transfer function [95], yielding the refractive index, \( n_s(\omega) \), and absorption coefficient, \( \alpha_s(\omega) \), optical parameters [93, 94]:

\[
n_s(\omega) = 1 + \frac{c \phi_{\text{sample}}(\omega) - \phi_{\text{reference}}(\omega)}{2\pi \omega d}
\]

\[
\alpha_s(\omega) = -\ln\left[ T(\omega) \frac{E_{\text{sample}}(\omega)}{E_{\text{reference}}(\omega)} \right] \frac{d}{d}
\]

with \( T(\omega) \) given as:

\[
T(\omega) = 1 - \frac{\left[n_s(\omega) - 1\right]^2}{\left[n_s(\omega) + 1\right]^2}
\]

In equation 3.5 the phase of both the reference and sample is needed to calculate the refractive index. This is obtained directly as the angle between the real and imaginary parts of the Fourier transform. This introduces a mathematical artefact where the polarity of the phase flips every \( 2\pi \). This is illustrated in Fig. 3.3 (c) and (d). Furthermore, sufficient strength in the THz \( \vec{E} \) field is required for accurate phase information. Regions of low instrument signal or high transmissive losses in \( E_{\text{sample}} \) introduce discontinuities in the phase spectrum. In Fig. 3.3 (d) and 3.4 these discontinuities are seen at frequencies corresponding to the high frequency cut-off introduced by sampling through a dielectric medium.

The phase wrapping every \( 2\pi \) must be overcome to correctly determine the samples optical parameters. This is achieved post-data acquisition with a simple mathematical adjustment. To unwrap the phase, an integer number of \( 2\pi \) is added at each wrapping point, giving the correct phase spectrum shown in Fig. 3.4.

Another important consideration is the spectral resolution. To reproduce a single discrete resonance in the frequency domain requires, in the time domain, a Fourier transform over infinity, not physically possible. Thus, the process of transforming from the time to frequency domain can introduce non physical phenomena
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Figure 3.3: Power and phase spectrum of dry air (red), in comparison to humid air (blue). Artefacts in the phase spectrum (d) are clearly observed in the low signal regions corresponding to water vapour absorptions present in (b).

Figure 3.4: Correctly unwrapped phases for dry and humid air. Artefacts from water absorptions and high frequency cut-off above 1 THz are evident in the phase for humid air.

into the final spectrum. A time ‘window’ is chosen in which to perform the Fourier transform over. This provides an absolute limit on the frequency domain resolution. Relating this to translation stage in the TDS setup gives a frequency resolution, $\Delta \nu$. 
of:

$$\Delta \nu = \frac{c}{2\Delta L}$$ (3.8)

Where $\Delta L$ corresponds to the traversed length of the delay stage. Alternatively, the time window can be chosen post measurement by truncating the time domain spectrum manually via proprietary software. Physical resonances are not delta functions, they have width giving a bound on the necessary resolution. Sampling over a large time-scale also introduces unnecessary noise, thus in taking appropriate data, a resolution between these bounds is chosen. This is illustrated in Fig. 3.5 where increasing the transformed time length from windows 1–3 better resolves water absorption lines, before the resolution limit is reached in windows 4–5.

**Figure 3.5:** Effect of moving the window integration position in the time domain on the resolution of the spectrum in the frequency domain. Water vapour lines are used for comparative analysis.

Free space spectroscopic measurements can pose a significant problem in the THz regime. Water vapour in the atmosphere contains a large number of substantial resonances in THz and IR frequencies [8, 96, 97]. These limit the spectral bandwidth in conjunction to introducing an added layer of complexity in extracting a true sample profile, with absorption strength proportional to the humidity (Fig. 3.6),
which is seldom consistent across measurements. Typically, THz-TDS measurements are taken in an environment either purged with dry air or nitrogen gas. Subsequently, the relative humidity surrounding the sample is minimised as are the water lines, exemplified in Fig. 3.6.

![Figure 3.6: Strength of spectral water lines with humidity in the sample environment. Sufficient reduction is observed when the humidity drops below 1%.](image)

Electrical noise is inherent to any system and can be viewed in taking a measurement with the THz beam completely blocked. This so called ‘noise floor’ is intrinsic to the instrument, providing a limitation on the smallest signal detectable. The ratio between the highest signal level with no sample and the root mean square of the noise floor is defined as the dynamic range (DR). A similar quantity, the signal to noise ratio (SNR), can also be used as a metric to investigate the electrical performance of a spectroscopic setup. This is defined as the ratio of the average signal with the root mean square of the noise.

TDS systems show a decay in signal strength with higher frequency [98]. Thus the DR is frequency dependent and introduces an upper limit to the absorption coefficient, $\alpha_{\text{max}}$ [98]:

$$\alpha_{\text{max}} d = 2 \ln[DR \frac{4n_s(\omega)}{(n_s(\omega) + 1)^2}]$$  \hspace{1cm} (3.9)
In any sample measurement with high losses where the signal approaches the electrical noise floor, the absorption coefficient will approach $\alpha_{\text{max}}$. If this threshold is reached, the absorption coefficient will follow $\alpha_{\text{max}}$ (3.7), dropping with higher frequency. The pseudo-decrease is an artefact of the system and not representative of any real phenomena.

Figure 3.7: Pseudo-decrease observed in a high absorbing sample close to equipment limitations. The blue curve gives the theoretical limit from equation 3.9, while the red line corresponds to experimental data obtained from a highly absorbing material.

3.1.1 Z-Omega Z2 Time Domain Spectrometer

The Z-Omega Z2 THz-TDS system (Fig. 3.1.1) is a ‘plug and play’ setup designed for ease of use. In this system optical elements are fixed in place and entire operation is controlled by external proprietary software. In this apparatus the pump/probe beam is generated via a Toptica FemtoFiberPro dual mode laser system, giving a 780 nm output. Beamsplitting is achieved via an indium tin oxide coated mirror. The pump beam is incident on a photoconductive antenna biased with a potential difference of 100 V. This gives an emitter current of 2.5 mA. Detection is achieved with a ZnTe crystal. The system is modulated at 12 kHz for lock in detection. With
this configuration the system generates a dynamic range of 70 dB and a bandwidth of 0.1–2 THz when purged with dry air or nitrogen gas. The time delay between the pump and probe beams is generated from a mechanical moving stage with a mounted retro-reflector. A single flip mirror (a) is positioned such that when lowered, an optical delay is introduced into the probe beam, equivalent to placing a sample 36 mm from the edge of enclosing box, allowing for reflectance measurements. In this geometry the first mirror in the THz beam is replaced with a silicon beamsplitter. Manipulation of the beam profile to small spot size on the sample and re-collimation
CHAPTER 3. EXPERIMENTAL METHODS

is achieved via two TPX lenses.

3.1.2 Advantest TAS7400TS Time Domain Spectrometer

Fig. 3.9 shows a schematic of an Advantest TAS7400TS TDS system used for higher frequency THz measurements. The Advantest system employs laser phase modulation for optical sampling, with ultra short 1550 nm pulses, as opposed to a mechanical delay stage. The pump and probe beams are optically coupled to respective photoconductive antennae used for THz production and detection. A pulse width of 50 fs is generated with an input power of 20 mW. An Advantest TAS1130 source module was used, exhibiting a bandwidth of 0.5–7 THz. This is a Cherenkov module that utilises non-linear optical crystal LiNbO$_3$ waveguides. An Advantest TAS1230 photoconductive antenna was used as the detection module. With this configuration the system generates a full scan range of 524 ps, a dynamic range of $\geq 60$ dB with an available resolution of 1.9 GHz. This system uses the rapid scan method in acquiring spectra.
3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is very similar in principle to TDS, in that a time domain signal is generated and Fourier transformed into a frequency spectrum. However, FTIR operation is based on the Michelson interferometer as shown in Fig. 3.10. Radiation, typically from a globar source [99], is split along two separate paths by a beamsplitter. One beam is reflected by a fixed mirror, while a second beam falls incident on a moveable mirror. The two beams are recombined at the beamsplitter, before partially falling incident on the detector. The translating mirror traverses a distance, \( \Delta x \), introducing a difference in the optical path (OP) of the two beams. Zero path difference (ZPD) occurs when the mirrors are positioned equidistant from the beamsplitter, resulting in constructive interference giving a global maxima in the interferogram.

Taking the simplest case in assuming a monochromatic source with intensity \( I_s \) and frequency \( \nu_s \) the intensity observed at detection, \( I_d \) will equal \( I_s \) when the
CHAPTER 3. EXPERIMENTAL METHODS

OP difference, \( x \), is equal to integers of \( 2\pi \). For any other value of \( x \), the detected intensity can be found via [100]:

\[
I_d(x) = 0.5I_s[1 + \cos(2\pi\nu_s x)]
\] (3.10)

Equation 3.10 assumes an ideal beamsplitter with 50% transmission and reflection. The non-ideality in any real beamsplitter must be accounted for. This is achieved by multiplying \( I_s \) by a frequency dependent factor reflective of the beamsplitter efficiency. Furthermore, the detection response will likely be non-uniform across all frequencies and also needs to be included in analysis. Finally, amplification and filtering present may also introduce frequency dependent modulation to the detected signal. In accounting for these we introduce a new intensity factor \( B(\nu_s) \), where \( B(\nu_s) \) is the intensity of the source modified by all the instrumental characteristics. Therefore the interferogram signal, \( S(x) \) is now found from equation 3.10 as:

\[
S(x) = B(\nu_s)\cos(2\pi\nu_s x)
\] (3.11)

To extend to a broadband continuous source, we integrate this equation:

\[
S(x) = \int_{-\infty}^{\infty} B(\nu_s)\cos(2\pi\nu_s x)d\nu_s
\] (3.12)

which is one half of a Fourier transform pair, with the inverse transform yielding the frequency dependent intensity:

\[
B(\nu_s) = 2\int_{0}^{\infty} S(x)\cos(2\pi\nu_s x)dx
\] (3.13)

Note that the factor of 2 and the shift of the lower integral limit to 0 is resultant of this being an even function. Equation 3.13 shows that, in theory, infinite resolution and bandwidth can be achieved. However, this is not practical as this would involve the moving mirror traversing from 0 to \( \infty \). Thus, limiting the scan length.
CHAPTER 3. EXPERIMENTAL METHODS

Figure 3.11: Typical interferogram detected with FTIR spectroscopy. Inset - Subsequent power spectrum obtained from the Fourier transformation of the time domain signal.

introduces an absolute maximum resolution of $1/2x$.

The experimental realisation of this theoretical process is shown in Fig. 3.11. Spectral acquisition occurs via two distinct methodologies, namely stepping and rapid scanning [99]. Stepping requires sitting the moving mirror at set values of $x$, and modulating the source with lock-in detection, while rapid scanning translates the mirror continuously and circumvents the need for source modulation. In the former case the SNR is determined via integration times on the lock-in amplifier, while in rapid scanning continuously obtained spectra are averaged with SNR determined by the number of scans.

3.2.1 Bomem FTIR System at the University of Wollongong

FTIR measurements were taken on Bomem DA8 Fourier transform spectrometer. This setup is technically an amalgamation of the DA8 and DA3.26 spectrometers, with functional parts present from both systems. The apparatus used is shown in
This system employs the blackbody radiation of a globar as a broadband source. Coupled with the option of a Si: bolometer and MCT detectors a total spectral range of 50–4000 cm\(^{-1}\) is available. This range can still be extended further with appropriate detection methods. Other source options (mercury lamp and white light) are available but not relevant to research in this thesis. The apparatus utilises the rapid scan acquisition method. Detected signal is sent to a pre-amplifier before being read by proprietary software. The final processed signal is a multiplication of the selected detector and amplifier gains. In minimising water vapour absorptions
and increasing the lifetime of some beamsplitters, the internals of the apparatus are maintained under high vacuum, only released for modifications in the sample chamber. Internal connections to a series of flip mirrors permit externally controlled transitions between transmission and reflection geometries.

For THz measurements, a KBr beamsplitter was used in conjunction to a helium cooled Si: bolometer. With this arrangement a full spectral range of 0.5–11.8 THz is present. Averaging over 100 rapid scans was found to be optimal in acquiring high quality spectra while remaining time efficient. The gains of the bolometer and pre-amplifier were kept minimal to remove unnecessary amplification of electrical noise. Investigated samples showed sufficient transmission not requiring higher amplification. Samples were mounted immediately before a light pipe coupled directly to the bolometer. This ensured a maximised detected signal.

3.2.2 Brüker FTIR System at the Australian Synchrotron

THz spectra at the Australian Centre for Synchrotron Science, is generated using a Brüker IFS 125/HR Fourier Transform Spectrometer. This interferometer consists of a 5 m scan length giving an available resolution down to < 0.0009 cm$^{-1}$. In conjunction, a broad spectral range from THz (5 cm$^{-1}$) to UV (50000 cm$^{-1}$) frequencies is available. Measurements taken at the Australian Synchrotron consisted of condensed phase transmission measurements from room temperature down to 6 K. A spectral region of 25–700 cm$^{-1}$ was accessed with the use of 6 $\mu$m and 75 $\mu$m mylar beamsplitters. A helium cooled Si:B bolometer was employed for detection.

The synchrotron light source consists of highly polarised radiation; elliptical for the bend magnet radiation and radial for edge radiation. The optical setup of the THz beamline results in an observed elliptical polarisation at the sample position biased towards the horizontal component.

Cooling was achieved via the use of a Cryo industries closed-cycle refrigerator system, equipped with diamond windows. In this system, up to four samples are mounted in thermal contact with a cold head and suspended vertically into the
synchrotron beam path. The sample chamber is filled with helium gas as a medium for heat exchange. Heat transfer occurs from the cold head/sample to the helium gas where it is subsequently pumped to a refrigeration unit, cooled and recycled. This process allows a base sample temperature of 6 K. A schematic of this system is presented in Fig. 3.13. Sample temperature control is achieved with the use of a small resistive wire for heating, externally regulated with standard PID controls.

In comparison to measurements in standard lab based systems; the synchrotron source has two distinct advantages. Firstly, the THz radiation emitted from the synchrotron beam is very intense. In fact, it is typically several orders of magnitude more intense than standard laboratory sources such as globars and mercury lamps. With similar detection and post-processing methods available to standard laboratories, the bright source gives a far superior dynamic range, ideal for samples exhibiting large absorption losses. Additionally, at the Australian Synchrotron the beam diameter is given to be $\sim 400 \, \mu m$, essentially a point source, resulting in a very high flux density. One sample emphasising the advantages of the synchrotron source is Linarite, a quasi-one dimensional magnet with a Néel temperature of 2.8 K [102], illustrates this point in Fig. 3.14. For this investigated sample, no useable signal could be found using the apparatus outlined in section 3.2.1, even with lock in detection and maximum signal. With the high flux synchrotron source a useable transmission is achieved, even when with signal diminished by the addition of a wire grid polariser. The advantage of the synchrotron source is emphasised further with the discovery of previously unforeseen resonant modes in this region.
Figure 3.13: Schematic diagram of Cryo-Industries 6K optical cryostat. Taken from [101].
Figure 3.14: Terahertz spectroscopy of linarite with synchrotron radiation unattainable with standard THz sources. Inset: Transmittance spectra showing characteristic absorptions and polarisation dependence.
3.3 Two Colour Wave Spectroscopy

Two colour wave spectroscopy, as the name suggests, involves producing electromagnetic radiation with two beams of lasing radiation with a slightly different wavelength or colour incident on a photomixer. This is called optical heterodyne or frequency mixing, as the THz output is the continuous wave beat of the two inputs. This methodology is attractive in the THz regime as photomixing with diode lasers presents the most cost effective source of THz radiation [103]. Multiple laser sources have been investigated including using two independent diodes or a singular two-colour laser based on either monolithic elements or cavity modes regulated in an external cavity [103, 104].

The photomixer substrate typically consists of low temperature grown GaAs (LT-GaAs) [105]. This semiconductor is well equipped for this application consisting a short carrier lifetime (<25 ps), high electric field breakdown (>5×10^5 V/m) and high mobility (>200 cm^2 V^−1 s^−1). Other semiconductor materials have been shown as appropriate photomixers for THz outputs, including LT-InGaAs [106]. Although, these may produce a higher THz output power, lower breakdown voltages present in these materials limit their lifetime and overall effectiveness. Overall implementation of the photomixer is varied, dependent on three factors [105]:

1. The optical continuous wave laser system generating the beat frequency

2. The electrode design converting the beat signal to an RF current

3. The design of the RF coupler

With two input laser beams incident on photomixer device, the corresponding delivery power of the beat frequency laser system is given by [104, 105]:

\[ P(t) = P_1 + P_2 + 2\sqrt{mP_1P_2}\cos(\omega t) \]  \hspace{1cm} (3.14)

Where \( P_1 \) and \( P_2 \) corresponds to the power of the individual input lasers, \( \omega = \omega_1 - \omega_2 \) is the frequency difference of the two inputs and \( m \) refers to the mixing
efficiency, dependent on the spatial overlap of the laser beams. Upon application of a bias voltage across the photomixer, photocurrent becomes modulated at the beat frequency, given by [104]:

\[ I(t) = I_0 \left[ 1 + \frac{2mP_1P_2 \sin(\omega t + \phi)}{P_0\sqrt{1 + \omega^2\tau^2}} \right] \quad (3.15) \]

Here \( I_0 \) is the DC photocurrent, \( P_0 \) is the average incident power where \( P_0 = P_1 + P_2 \). \( \tau \) corresponds to the carrier lifetime of the chosen photoconductive material and \( \phi \) denotes a carrier lifetime dependent phase shift. Finally, with a coupled antenna translating the final THz wave into free space, the total THz output power, \( P_{THz} \) can be found:

\[ P_{THz}(\omega) = 2I_0^2 R \frac{mP_1P_2}{P_0^2[1 + (\omega\tau)^2][1 + (\omega R A C)^2]} \quad (3.16) \]

A schematic of the two color system used in this research is given in Fig. 3.15. Here THz is generated by a continuous wave, quasi-monochromatic photomixer system. The photomixer is biased from 0–20V and is pumped by two fiber coupled near infrared (NIR) diode lasers (Toptica DL-100), offset in frequency. The laser difference frequency is measured by an Advantest Q8384 fiber coupled optical spectrum analyser (OSA) monitoring the laser modes. Adjusting the frequency difference of the lasers allows for THz tuning from 0.1–1.0 THz (Fig. 3.16). The laser outputs are combined in a fiber optic cable which is subsequently coupled to an amplifier system. In turn, the output from the amplifier is coupled directly to the photomixer. In this configuration optical power up to 150 mW is achievable. The lasing frequency exhibits temperature dependence, the tool utilised in tuning the THz output. Spectral acquisition involves holding one diode at a fixed temperature, hence frequency, while systematically altering its offset counterpart, shifting the relative beat frequency. Additionally, the output frequency is also proportional to the diode current. Altering the current permits a much higher spectral resolution in the vicinity of 100 MHz, with standard measurements operating with resolutions
in the 0.5–2 GHz region. The laser control system and lock in amplifier is externally manipulated by computer software developed in LabView.

One issue in acquiring a THz spectrum is the time delay introduced in measuring the beat frequency on the OSA at every sampling point. Doing so increases measurement times beyond reasonable limits, especially considering a time-limited helium cooled bolometer is usually employed for detection. Navigating this issue generates a minor artefact in the final spectrum. The shift in laser frequency is, to a high approximation, linear thus the OSA is employed to measure only some points at set intervals throughout the scan. Post processing will hence involve linearly interpolating between the known frequency points. Choosing this parameter is an option in external software.

Figure 3.15: Two colour system used for THz spectroscopy from 0.06–1 THz. Graphic created by E. Constable.
Figure 3.16: THz spectrum generated by two colour wave photomixing.
3.4 Powder X-ray Diffraction

Figure 3.17: Schematic of equipment used in x-ray diffraction.

X-ray diffraction (XRD) is an important tool used in the identification of crystalline solids, fundamentally based on the wave properties of the x-ray photons. A schematic of a typical XRD setup is shown in Fig. 3.17. Here a high voltage in the x-ray tube ejects electrons, which collide with a metal target. X-rays are emitted which are collimated into a singular beam as well as having undesired wavelengths filtered out. The collimated beam is directed onto the sample, subsequently producing an interference pattern where maxima are measured by a rotating detector.

In its simplest form, X-ray diffraction is best described by Bragg’s law [107]

\[ n\lambda = 2dsin(\theta) \]  

Equation 3.17, while simple enough, assumes a highly crystalline, anisotropic sample. In extending this theory into powder x-ray diffraction, a more meticulous analysis is required. In this case, powder samples result in random orientation of the crystal planes, making them isotropic. If we assume the sample is truly isotropic then
scattering will occur off each atomic (hkl) plane simultaneously and in all directions. Subsequently reflected x-rays will form a series of concentric cones, which in a two dimensional plane form so called Debye-Scherrer rings [108]. These are radially symmetric about the propagation axis of the incident x-ray beam. From Bragg’s law, these cones subtend an angle $2\theta$ from the sample position corresponding to a reciprocal lattice vector $\vec{G}$, with length $q$ defined by the following:

$$|\vec{G}| = q = 2k\sin(\theta) \quad (3.18)$$

Where $k$ is the momentum transfer vector equivalent to $2\pi/\lambda$. Here, $\theta$ refers to half the full scattering angle subtended by the cone of x-ray radiation reflected by the sample.

An important consideration is the need for a well defined, discrete wavelength of x-rays. This is achieved by using characteristic x-ray radiation (Fig. 3.18), commonly the CuK$_\alpha$ line[109], with a wavelength of 0.15418 nm. To ensure signal clarity, the K$_\beta$ line as well as the enveloping bremsstrahlung radiation is filtered out before the radiation leaves the x-ray tube.

![Figure 3.18: X-ray emission spectrum obtained from a copper target.](image)

Powder x-ray diffraction (PXRD) measurements made in this thesis were done so using a GBC Mini Materials Analyzer (MMA) XRD setup. CuK$_\alpha$ radiation is
used for measurements, detected via a Xe proportional detector tube and graphite monochromator. This setup permits intensity peaks to be acquired through a full 0–90 degrees bragg angle. The detector incrementally steps through a desired angular range, waiting at each point for sufficient signal. Visual XRD proprietary software is used to interface with the setup. Another software package with accompanying databases, Traces, is used to analyse PXRD data obtained through Visual XRD. An experimental resolution of 0.02 degrees was chosen for PXRD measurements made throughout this thesis.
Chapter 4

3D Printing in the Terahertz Regime

4.1 Introduction

This chapter will explore the feasibility of a range of 3D printed materials used primarily in fused deposition modelling, the most common, versatile and easily accessible form of 3D printing. Optical properties of the materials used will be characterised in the THz regime and assessed on their feasibility for use in THz devices. This analysis will also account for the overall printability of the materials as well as their mechanical rigor. Subsequently, the chapter will explore results obtained for some 3D printed THz diffraction gratings and lenses and finish by analysing the printing process of a much more complicated device: a 3D printed hollow-core hyperuniform waveguide.

4.2 Filament Characterisation and Printability

4.2.1 Experimental

Experiments in this section were performed on a Makerbot Replicator 2X: Experimental 3D printer (Fig. 4.1). This printer was chosen specifically for this task for
the following reasons. Firstly, the printer had to be placed at a price point easily accessible for research labs while maintaining the core advantages of 3D printing in the THz: cost effectiveness and customisation. The Replicator 2X is designed specifically with this in mind. The printer contains all of the hardware required to print the full range of filaments, while allowing high levels of user input in easily modifying, exchanging and upgrading working parts as required for printing with exotic filaments. This is coupled with high levels of access to the printer’s source code, permitting adjustments to all possible print parameters; ideal for printing with non-standard filaments. Most inexpensive 3D printers are designed specifically for one type of filament, with print parameters optimised accordingly, without access for manipulation. Typically, these printer manufacturers also seal many of the working parts such that modifying them to print non proprietary filaments results in a void of warranty and high risk of serious damage.

The Replicator 2X is built on a powder coated steel frame allowing a build volume of 24.6 cm × 16.3 cm × 15.5 cm. Fine stepper motors give a nozzle XY positioning
precision of 11 µm and a Z axis positioning precision of 2.5 µm. Consequently, a high resolution layer height of 100 µm is available for printed parts. An aftermarket print arm stabilisation kit was fitted to the printer resulting in a more stabilised build plate. With this upgrade, the minimum layer height is improved to 50 µm. These can be seen as the red arm along the build plate in Fig. 4.1. 0.4 mm nozzles were used for extrusion. This also provides the limiting resolution (0.4 mm) in a final print, which has been verified experimentally. Dual extruders are present in this setup, allowing prints with different materials. The printer also boasts a heated build platform, needed for filaments with high coefficients of thermal expansion, to prevent warping and to assist in parts adhering to the build plate.

18 common and exotic filaments were obtained for investigation including: polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), nylon, polycarbonate (PC), polypropylene (PP), polyethylene terephthalate (PET), high impact polystyrene (HIPS), and polyvinyl alcohol (PVA) with their corresponding modifications and blends. Where possible, pure filament was obtained free from colorising agents and dyes.

The optimal build parameters for each filament were found experimentally from trial and error using manufacturer recommendations as a starting point. These are summarised in Table 4.1. Prints were found to be optimal with the following considerations. Firstly, the model dimensions were precisely measured with calipers to ensure the absence of under or over extrusion. Bed temperatures were optimal when minimal or no warping with good bed adhesion was present. Extrusion temperatures were optimised by monitoring test prints, finding where silky, smooth strips of laid material were present with no air pockets and high homogeneity. In the cases where a range of successful extrusion temperatures were present, samples were printed at the highest possible temperature. This enables better merging between adjacent strips of laid thermoplastic, thus higher homogeneity of the plastic throughout the sample. This reduces scattering of the THz waves from individual strands of printed material.
Table 4.1: Optimised filament print parameters.

<table>
<thead>
<tr>
<th>Filament</th>
<th>Modification</th>
<th>Extrusion Temperature (°C)</th>
<th>Build Plate Temperature(°C)</th>
<th>Min Layer Height (mm)</th>
<th>Print Speed (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>Standard</td>
<td>190–210</td>
<td>Not needed</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>PLA/PHA blend</td>
<td>190–210 C</td>
<td>Not needed</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td>ABS</td>
<td>Standard</td>
<td>230</td>
<td>110</td>
<td>0.05</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Conductive ABS</td>
<td>230</td>
<td>110</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>Nylon</td>
<td>Standard (white)</td>
<td>230–250</td>
<td>70–100</td>
<td>0.1</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>645</td>
<td>230–250</td>
<td>70–100</td>
<td>0.1</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>910</td>
<td>245</td>
<td>70–100</td>
<td>0.1</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Bridge</td>
<td>230–250</td>
<td>70–100</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>PCTPE</td>
<td>230</td>
<td>40</td>
<td>0.1</td>
<td>70</td>
</tr>
<tr>
<td>PC</td>
<td>Standard</td>
<td>&gt;300</td>
<td>&gt;120</td>
<td>0.1</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>PC/ABS blend</td>
<td>&gt;275</td>
<td>&gt;120</td>
<td>0.1</td>
<td>45</td>
</tr>
<tr>
<td>PP</td>
<td>Standard</td>
<td>250–280</td>
<td>&gt;120</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>PET</td>
<td>T-Glase</td>
<td>240</td>
<td>&lt;68</td>
<td>0.1</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Colorfabb-XT</td>
<td>240–260</td>
<td>60–70</td>
<td>0.1</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>PETG</td>
<td>215–235</td>
<td>Not needed</td>
<td>0.1</td>
<td>60</td>
</tr>
<tr>
<td>HIPS</td>
<td>Standard</td>
<td>230</td>
<td>110</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td>PVA</td>
<td>Standard</td>
<td>160–190</td>
<td>Not needed</td>
<td>0.1</td>
<td>10</td>
</tr>
</tbody>
</table>
Samples for spectroscopic purposes were designed as $50\text{mm} \times 50\text{mm} \times 10\text{mm}$ squares. The geometry was found to be optimal for mounting in THz-TDS equipment, while providing suitable transmitted signal for characterisation measurements across a large frequency range.

Furthermore, it is imperative to have consistency across measured samples to draw direct comparisons. As such, all printed samples were ensured to have equal thickness and dimensions. Additionally, the fill pattern, external shells and post processing was consistent across all measured samples. In terms of measurement, all instrument parameters were maintained across samples, as outlined below to further ensure accurate comparisons in the results.

Transmission spectra were taken on a Z-Omega Z2 THz time domain spectrometer. The sample environment was purged with dry air. Two sensors inside the system ensured the humidity was below 0.1% before commencing measurements. A total scan distance of 10 mm was chosen. This gave a suitable resolution (0.02 THz) while simultaneously avoiding signal from back reflections. A scan speed of 0.01 mm/s was chosen as the fastest available without effecting data quality.

Transmission spectra were verified using an Advantest TAS7400TS time domain spectrometer. As previously, the experimental apparatus was purged with dry air. A preset spectral resolution of 15 GHz was chosen. 16384 rapid scans were averaged to produce the final THz spectrum.

### 4.2.2 Polylactic acid

Polylactic acid (PLA) is one of the most commonly used thermoplastics in 3D printing. The main reasons for this are twofold: Firstly, PLA is *eco-friendly*, being biodegradable and derived from natural products such as corn, sugar cane and potatoes [110]. Thus, PLA is seen as a sustainable alternative to petroleum based polymers across many applications [111]. Furthermore, PLA uses 25–55% less energy in production than its petroleum derived counterparts [112]. Secondly, PLA’s thermal properties are well suited to 3D printing. A relatively low glass transi-
tion temperature of 60°C and melting point of 153°C [113] allows printer extrusion temperatures of around 190°C, easily accessible by all commercial 3D printers. Additionally, a relatively low thermal expansion coefficient of $70 \times 10^{-6} \, {\text{C}}^{-1}$ [114] gives negligible warping of printed models and circumvents the need of a heated print bed. Consequently, PLA is the easiest and most popular filament to print with. In terms of THz printing, PLA’s toughness is its only downside. PLA prints will be very brittle, consequently limiting applications where high stress is present [112]. This will pose problems for prints in a laboratory context where, for example, a part may need to be fixed rigidly to an optical bench. However, since THz 3D printed devices are predominately optical in nature, this will generally not be an issue, especially considering the relative fragility of many current optical THz components such as beamsplitters.

To date, many approaches have been taken to improve PLA’s mechanical properties, including various types of copolymerisation and blending. The latter of these accounts for most efforts in improving PLA [112]. Poly(hydroxyalkanoate) (PHA), an aliphatic polyester produced by micro-organisms, has been found to drastically improve toughness upon blending with PLA. The PHA has the effect of lowering the melting point and overall crystallinity of the polymer structure, leading to an increase in toughness. One study [115], showed an increase in energy-to-break toughness of PLA when blended in a 90/10 ratio (per weight) with PHA from $\sim 0.25 \, \text{Nm}$ to $\sim 2.0 \, \text{Nm}$. This dropped to $\sim 1.4 \, \text{Nm}$ with a 80/20 ratio before, interestingly, reducing back to $< 0.25 \, \text{Nm}$ for PHA content above 40%. The amount of blended PHA was not given for the filament tested here. This was also unavailable from direct request of the manufacturer. It is safe to assume the PHA content is below 20% by weight.

Fig. 4.2 shows the absorption coefficient of PLA and PLA/PHA blended 3D printer filaments in the THz regime. The absorption curve is featureless, increasing strongly with frequency, as is common in this region for dielectric materials. The standard and blended PLA filaments have identical spectra in this region.
Fig. 4.3 interestingly shows that despite the similar absorption, the refractive index of each filaments differ. For PLA the refractive index is $1.56 \pm 0.02$ across the spectrum. For PLA/PHA blended filament this shifts to $1.64 \pm 0.02$. Both filaments appear to have a slight decrease in refractive index across the frequency range. This is consistent with the THz data shifting towards the visible refractive index of PLA calculated as $1.465$ at $589$ nm from the sodium D-line [116].

The transmissive properties of the blended filament are dominated by the PLA.
No change in the absorption coefficient is present despite a mixture of 10–20% PHA. It is only in the refractive index that the differing filament composition is revealed. Thus, for 3D printing of transmissive optical devices for THz applications, the filaments are identical. Considering the more desirable mechanical properties of the PLA/PHA blend, this filament becomes the better option for this task.

However, the overall use of these filaments in the THz regime is still limited to thin devices and low photon energies. From Fig. 4.2 a bulk material of only 1 cm thickness results in over 99% transmissive losses for frequencies above 0.8 THz. For any frequency above this, these filaments are not feasible for optical applications. Below 0.5 THz, with the absorption coefficient dropping below 10 cm\(^{-1}\), thin optical devices, such as diffraction gratings are achievable. Lenses and other applications that require a bulk of material will still be largely ineffective in this region without more complicated design. For example, removing the bulk of a standard lens in a fresnel lens.

In terms of the printability, PLA and PLA/PHA are at the forefront. The addition of PHA has no appreciable effects in the ease of printing models when compared to standard PLA. Altering print parameters such as extrusion temperatures and feed rates was found to be unnecessary when changing between the two filaments. Overall, both filaments are easily printed. No heated bed is required due to low thermal expansion and models will stick to almost any build surface. Hence, printing accurate geometries, as is desirable for optical THz elements, is comparatively very easy. This is reflected in the use of PLA in almost all entry level 3D printers with novice users in mind. This is advantageous when considering that thin and precise components need to be printable for these filaments to be of use in 3D printing functional THz optics.

### 4.2.3 Acrylonitrile Butadiene Styrene

Acrylonitrile Butadiene Styrene (ABS) is a very commonly used amorphous thermoplastic polymer. ABS consists of highly desirable mechanical properties, which
drive its large use as a 3D printer filament. Alongside PLA, ABS is the most popular filament used in FDM 3D printers. ABS is a tough, stiff polymer that also exhibits chemical, heat and moisture resistance [117]. In turn, 3D printed ABS parts extend beyond novel models and prototypes into structural components for equipment such as drones [118]. Despite the superior mechanical properties, ABS polymer is not biodegradable as is the case for many of its competitors. This has spearheaded research into deriving 3D printable polymers with the mechanical properties of ABS, but the environmental properties of PLA [119].

Thermally, ABS has a desirable glass transition temperature of 112.6°C [120] leading to extrusion temperatures typically in the range of 230°C, well within the capabilities of all FDM 3D printers. Unfortunately, a thermal expansion coefficient of $100 \times 10^{-6}$°C results in prints susceptible to warping. Consequently, printing in ABS requires the use of a heated print bed, in the vicinity of 110°C in conjunction to good bed adhesion to navigate this issue. Bed adhesion is improved by printing on polyimide (kapton) tape as well as preparing the build surface with glue, hairspray or a thin layer of acetone.

Although ABS polymers, like many plastics, have the desirable property of a high intrinsic electrical resistance, many applications would benefit from electrically conductivity. Accordingly, research has lead to the development of polymer complexes with enhanced conductivity compared to their original composition. This is typically achieved through blending polymeric materials with a conductive filler, such as metal fibres and carbon [121]. This would be desirable for FDM printing, as such an experimental carbon-blended ABS has been developed, sold under the proprietary name ‘Conductive ABS’.

Fig. 4.4 gives the absorption coefficients for ABS and conductive ABS filaments. Standard ABS shows a steady increase with photon energy with an absorption of $< 10 \text{ cm}^{-1}$ below 0.75 THz rising to $> 40 \text{ cm}^{-1}$ above 1.7 THz. Besides this, the spectra is featureless for this filament. A significant increase in absorption is present for conductive ABS filament, as expected for conducting materials. The absorption
coefficient remains above $30 \text{ cm}^{-1}$ at low frequency, sharply reaching $> 100 \text{ cm}^{-1}$ beyond $0.8 \text{ THz}$. At this point, the data is cut-off as the highest absorption coefficient measurable by the system is reached. Furthermore, the small transmissive window corresponds to the lowest dynamic range available in the experimental setup, hence the low signal to noise for this sample.

In Fig. 4.5, the refractive indices for standard and conductive ABS are $1.49 \pm 0.01$ and $2.19 \pm 0.08$ respectively. As expected, the conductive variant shows an appre-
ciably higher refractive index, above the range typical for bulk dielectric materials. The refractive index for conductive filament shows a slight decrease with frequency, while standard ABS is steady across the THz range.

In terms of 3D printing optics for the THz region, standard ABS shows some promise. The absorption coefficient is $<$ 10 cm$^{-1}$ for frequencies below 0.75 THz and approaches 5 cm$^{-1}$ in the 0.4 THz region. Thus, useable transmission is found in this region for the production of quasi-optics.

Despite the claim, the overall conductivity of the conductive ABS filament is quite poor, given as $1 \times 10^{-4}$ S/m, somewhat in the ‘mid-range’ between plastics and conductors. This limits its use for THz devices. The conductivity is increased enough from standard ABS to effect the optical spectrum to the point of rendering these devices unfeasible, but not enough to open up applications in printed devices such as reflective optics and waveguides, typically engineered from metals. Despite this, the improvement in conductivity from standard ABS is encouraging.

ABS’ printability is generally fairly easy provided the 3D printer contains the required hardware. A heated print bed is the minimum requirement, with a closed print environment desirable to minimise warping issues. For most novice users, slight warping may not be an issue, but for printing functional THz optics this will become a significant problem, especially if the structural changes with cooling are not uniform. This implies a careful print setup with detail taken in optimising print parameters for each device is necessary. This requires more than a basic level of user expertise. Thus, successful prints with high geometric precision are feasible for the THz regime below 0.75 THz, but care must be taken in the print and design process.

Further issues arise for conductive ABS when printability is considered. Generated models are ‘chalky’ in appearance with smooth, accurate designs not feasible, with a limiting resolution of 2 mm, observed experimentally. Smoothing models post-production can improve this problem, but is not sufficient for designs with internal structures. Also, fine particles of carbon are released into the air during prints. These can be found deposited over the printer after some time, questioning
the effects on the lifetime of moving parts. Hence, safety issues arise in breathing in these particulates, forcing prints to be performed in well ventilated areas or fume hoods. Factoring the required resolution for conductive THz devices, like resonators and metamaterials, is well below those available with this filament, with the outlined safety concerns; it is concluded that conductive ABS shows poor prospects in 3D printing functional THz devices.

4.2.4 Nylon

Since the inception of FDM 3D printing technology, nylon has steadily become more accessible and functional as a filament. Standard nylon filaments are notoriously difficult to print with for many reasons: Firstly, relatively large thermal expansions ranging from \((8-10) \times 10^{-5} \, ^\circ C^{-1}\) for polymers suitable for 3D printing result in large warping issues for printed parts. This is exaggerated by high print temperatures above \(250^\circ C\) required for successful nozzle extrusion. Secondly, layer adhesion and overall strength is poor due to the lack of compression provided by FDM printers. In industry, the strength and desirability of these nylon polymers is realised in the compression involved in the injection moulding process. This is simply not achievable with a filament 3D printer [122]. A more general issue with nylons, that extends across industry, is its large water absorption. For example, for standard nylon-6, a 2.7% equilibrium water absorption and 9.5% saturation level was observed at 50% relative humidity [123]. In response to these issues, a series of nylon filaments have been developed, each aiming to minimise one or all of these issues, while filling a certain niche in desirable mechanical properties. To investigate THz characteristics, plain white nylon filament was obtained as well as a series of engineered variants developed by taulman3D [122]:

- **Nylon 645** - Produced to increase polymer bonding, reduce thermal expansion effects while maintaining high chemical resistance.

- **Nylon 910** - Engineered to meet high performance needs. Minimises thermal
expansion beyond Nylon 645, gives a large range of chemical resistance while simultaneously consisting of a very high tensile strength.

- **Bridge Nylon** - Modified variant of Nylon 645. Aimed at increasing print bed adherence, reducing water absorption and thermal expansion while remaining transparent for applications in non destructive testing of the internal structures in 3D printed models.

- **PCTPE** - Plasticised copolyamide thermoplastic elastomer is a chemical blend of nylon with thermoplastic elastomer (TPE), aiming to produce a more user-friendly flexible model filament that maintains the positive mechanical durability of nylon.

![Figure 4.6: Absorption coefficients of nylon based 3D printer filaments.](image)

Nylon filaments show the standard increasing absorption with frequency in the THz region, as can be seen in Fig. 4.6. No absorption peaks are observed across the spectrum. Overall, the absorption of these filaments is considerably high. For frequencies above 0.75 THz the absorption coefficient is $> 20 \text{ cm}^{-1}$ rising significantly, rendering optical devices in this region unusable. For frequencies below 0.75 THz, the absorption does steadily drop, but insufficiently to be considered a candidate for wide range applications in THz optical devices. Even at the lowest point, the
transmissive losses per cm of bulk are still above 75%, forcing any printed optics to have interaction lengths of a few millimetres at most.

Interestingly, the spectra are similar for all the nylon variants, despite the changes in composition, production and in the case of PCTPE, blending with another polymer. This suggests that the nylon base dominates the spectral profile. Furthermore, it can be concluded that TPE is relatively transmissive in the THz regime, at least in this form. Importantly, the spectral consistency across the filaments permits end users to choose a product based on their specific requirements without sacrificing optical properties.

![Wavenumbers (cm⁻¹)]

**Figure 4.7:** Refractive index of nylon based 3D printer filaments.

As expected, the pure nylon based filaments share similar refractive indices. From Fig. 4.7 white nylon has a refractive index of 1.75 ± 0.03 across the spectrum. 645 and 910 modifications show refractive indices of 1.75 ± 0.01 and 1.71 ± 0.01 respectively, with bridge having a 1.70 ± 0.01 refractive index. PCTPE is somewhat lower at 1.61 ± 0.01 for THz frequencies. Unlike the absorption coefficients, the refractive indices reflect the subtle changes in the nylon filaments as well as the more substantial modification in the PCTPE filament. The refractive index for 645, 910, bridge and white nylon show a subtle drop with increasing frequency. PCTPE is not consistent with this, appearing constant across the range. For visible photons,
the refractive index of these nylons will fall in the range of 1.50–1.53, depending on the exact modification [116]. The THz data is in agreement with this, with the higher refractive index materials dropping towards this region. PCTPE, whose THz refractive index is much closer to the visible case, remains constant.

Overall, printing with plain nylon is very difficult, as outlined previously in this section. Testing plain white nylon confirmed this, with tests peeling off the print bed even with initial layers being glued down with an acetone-ABS slurry. However, the modified variants were found to be a marked improvement and are somewhat similar in print difficulty to ABS. Printing will require a heated print bed around 70°C and a hot end capable of producing extrusion temperatures in the vicinity of 250–260°C. For extending prints into THz devices, the mechanical properties are suitable for the modified 645, 910, bridge and PCTPE variants. Considering 910 and bridge are improvements on 645, while being optically identical, they would be the better equipped to produce THz optics. Despite this, when considering the required hardware, user experience and high absorbance, nylon filaments are generally unsuitable for THz devices across the spectrum save for small, niche applications.

4.2.5 Polycarbonate

Polycarbonate is somewhat of a niche filament for 3D printing applications. It consists of very desirable mechanical properties including superior toughness and impact resistance over all other 3D printer filaments. This is offset however, with polycarbonates thermal properties, which make it a very difficult to use. Polycarbonate has a relatively high glass transition temperature of 150°C, which implies high extrusion temperatures in the 3D printing process, typically 300°C. Furthermore, polycarbonate has a high linear thermal expansion coefficient of $70 \times 10^{-6}$ °C$^{-1}$ [124]. The coupling of these two thermal properties leads to large warping of prints in conjunction to pushing standard commercial 3D printer hardware to the limits of operation. Suppliers quote the required temperature for the print bed to be ‘as high as possible’ further illustrating the extreme setups required to produce
successful models.

As with many other filaments, blending of polycarbonate has been attempted to reduce harsh printing conditions. Typically made with ABS, attention is required to optimise mechanical properties while sufficiently improving thermal properties. For these blends the optimal in mechanical properties is found for a polycarbonate concentration of 90% [125]. Experimental data has shown that outside this 90/10 ratio most mechanical properties are weaker than both pure ABS and polycarbonate. This is the most likely ratio of the filament used in this study, however details have been omitted by the supplier and refused upon request. As such, concrete conclusions cannot be drawn in regards to the precise composition.

![Figure 4.8](image)

**Figure 4.8:** Absorption coefficient of polycarbonate and polycarbonate/ABS blended 3D printer filaments. Standard ABS is also shown for comparative purposes.

Experimental data in Fig. 4.8 shows desirable optical properties in the THz region for standard polycarbonate filaments. The absorption coefficient is below 10 cm\(^{-1}\) for frequencies below 1 THz before further dropping below 5 cm\(^{-1}\) for frequencies below 0.7 THz. Thus 3D printed quasi-optics for THz applications are achievable in the < 0.7 THz range, while thin dielectric devices are still feasible up to 1 THz. Above 1 THz absorption losses steadily increase and become too high to be suitable for THz applications.

The polycarbonate/ABS blended filament shows a significant increase in absorp-
tion across the spectrum. In this case the absorption coefficient only drops below $10\,\text{cm}^{-1}$ for frequencies less than 0.8 THz and fails to fall below the 5 cm$^{-1}$ threshold. As expected, with higher photon energy the absorption increases. From the experimental data, the added ABS serves to dominate the optical spectrum, with the spectral profile consistent with standard ABS until 1.5 THz. Both the standard and blended filaments are featureless across the spectrum.

![Graph](image)

**Figure 4.9:** Refractive index of polycarbonate and polycarbonate/ABS blended 3D printer filaments.

The refractive index of the standard polycarbonate is observed to be $1.49 \pm 0.03$. With ABS showing a similar refractive index of $1.49 \pm 0.01$, the blended filament gives the expected result of $1.51 \pm 0.01$, agreeing within experimental uncertainty, as can be seen in Fig. 4.9. Standard polycarbonate hints at a very slight decrease in refractive index with frequency. This is emphasised by the gradual separation of the standard and ABS blended curves. This is not in agreement in comparison to the visible light refractive index of polycarbonates, given as 1.53–1.59 [116]. This suggests a local minima must be present for the polycarbonate filament between the THz and visible regions of the electromagnetic spectrum.

Optically, pure polycarbonate filament shows promise in 3D printing THz optics up to 1 THz. Unfortunately, this is diminished with the blended filaments with the ABS mix increasing the overall absorption to the same as standard ABS filament up
to 1.4 THz. Thus, in this region, given that ABS is far easier to print with it would be a much better choice. Above 1.4 THz there is a slight decrease in the blended filament curve compared to the ABS, but the overall absorption losses are so severe that this filament is not usable in this range.

The downside to using polycarbonate for THz applications is the extreme print conditions. High levels of user expertise are essential for successful prints with this filament. The extrusion temperature of 300°C is outside the capabilities of standard commercial systems, and will melt the PTFE tubing between the filament drive gear and heater block. Some level of avoidance of this problem can be achieved by lowering the extrusion temperature below the ideal. Polycarbonate changes phase over a large temperature range so extrusion can be achieved as low as 275°C. To offset the temperature drop, a slower print speed must be selected. These work against each other when thermal expansion is factored. A slow print speed allows parts more time to cool and exaggerates already significant thermal expansion. Ideally, prints need to be performed at higher temperatures and faster. Some level of warping is unavoidable with polycarbonate. This can be minimised with a very high bed temperature \( > 130°C \) and by physically sticking prints to the build plate with an ABS slurry. However, test prints of lenses showed that after some time the edges would still warp and pull the surface layer off the build platform.

Overall, pure polycarbonate is a viable candidate for THz optical applications provided sufficient hardware and user experience is available. The mechanical properties are ideal for delicate and fine elements and a reasonable transparency window is available to take advantage of. Large thermal expansion limits the most successful prints to ones smaller in size and with high degrees of rotational symmetry. Furthermore, if the mechanical properties of the THz device are not so important, other filaments discussed provide comparable and better optical properties while being much easier to use, thus being more suitable for 3D printed THz equipment.
4.2.6 Polypropylene

Polypropylene is generally considered an experimental 3D printer filament. Despite this, development of a useable filament for FDM printers is desirable owing to large array of applications and consummation in society. Polypropylene is considered a tough plastic with the desirable attributes such as fatigue resistance and low friction. This makes a prime candidate for use in hinges, gears and contacting surfaces. Polypropylene also consists of decent chemical resistance seeing applications in packaging for cleaning products and other liquid containers. Polypropylene has a large thermal expansion, with a linear coefficient of $200 \times 10^{-6}\text{C}^{-1}$. A 0°C glass transition temperature and $\sim 130°C$ melting point leads to extrusion temperatures in the vicinity of 230°C. However, successful print temperatures are highly variable between setups due to the current experimental nature of the filament.

![Figure 4.10: Absorption coefficient of polypropylene 3D printer filament.](image)

Experimentally, polypropylene filament continues the trend showing a steadily increasing absorption with frequency as shown in Fig. 4.10. The spectral envelope is featureless. A useable region is observed below 0.6 THz with the absorption coefficient dropping below 10 cm$^{-1}$. This further drops below 5 cm$^{-1}$ for frequencies below 0.4 THz suggesting viability for diffractive optics in this region. Above 0.6 THz the absorption becomes too great to print optics devices, with transmissive losses above
Although, the overall absorption of polypropylene is somewhat less than many other filaments investigated in this chapter, it is still significantly higher than expected. In [126] the absorption coefficient of a polypropylene filament is given to remain close to $0 \text{ cm}^{-1}$ across the same spectrum as presented here. Two possibilities are attributed to this discrepancy. Firstly, a possible error in the experimental setup. For this sample, generating consistent, homogenous specimens for spectroscopic purposes was difficult. However, numerous geometric shapes and multiple measurements were performed across many samples and found to give consistent results. So it is not likely that this is the origin of the abnormally high absorption. This is further backed up by the same process generating consistent expected results for all other tested filament samples. Secondly, and likely the origin of this discrepancy, is the actual composition of the filament is not entirely polypropylene, or at least a different modification to other tested polypropylene materials. The manufacturers specifications do not give definitive data pertaining to any blending, or true composition, of the filament. It is merely sold as a proprietary homopolymer polypropylene filament. Given the extreme print conditions required for polypropylene it is likely the supplier has added other material like ABS, or developed a unique filament modification, to try and reduce these issues. As can be seen in Fig. 4.8 for polycarbonate, blending with other thermoplastics can significantly alter the optical properties and in Fig. 4.12 the same is observed for filament modifications in PET.

Fig. 4.11 shows a consistent refractive index of $1.48 \pm 0.01$. This is flat across the spectrum and is close the refractive index of 1.495 calculated in [126]. Interestingly, this slight change is further evidence of the previous hypothesis that this polypropylene is modified, as other tested filaments showed similar small changes in the refractive index between base and altered variants. Figs. 4.13, 4.3 and 4.7 illustrate this phenomenon in PET, PLA and nylon blended/ altered filaments. The refractive index for polypropylene is constant for THz frequencies. Interestingly, this agrees with the refractive index of polypropylenes in the visible spectrum of
In terms of the printability for THz devices, despite viable optical properties, polypropylene is not feasible as a filament in FDM printing of THz components. This boils down to the thermal properties of the filament. The large expansion makes prints almost impossible. Only small fast prints with a single axis of rotational symmetry are possible, and even then they are extremely difficult. Test prints with the edges physically glued to the build platform were observed to bubble at the centre, consequence of the extreme warping. Furthermore, any geometry of desired THz prints would be difficult to reproduce accurately, further adding to the case against using polypropylene filament. Other thermoplastics tested show advantages in optical and mechanical properties as well as ease in the printability process.

### 4.2.7 Polyethylene Terephthalate

Polyethylene Terephthalate (PET) is commonly used in the manufacturing of plastic bottles. It is a transparent, fairly hard material, with its transparency changing as it is heated and cooled in the 3D printing process [127]. The wide use and visible transparency of the thermoplastics make it an attractive candidate as a 3D printer filament. Not just visually appealing, the optical clarity is ideal in non
destructive analysis of the internal structure of models, giving insights highly sort after in the prototyping process. The thermal properties of PET also make it an attractive printing filament; with a glass transition temperature of 75°C allowing print temperatures in the vicinity of 230–260 °C [128]. With a thermal expansion coefficient of $59 \times 10^{-6} \, ^\circ\text{C}^{-1}$, lower than most printer filaments, warping is a minimal issue with this thermoplastic. PET can be modified through copolymerisation and as such, like with many filaments, proprietary modifications have been made to improve the overall print properties. These include using PETG (glycol modified PET), as well as manufacturer developed filaments like Taulman T-Glase (PETT) and Colorfabb-XT. The exact composition of these filaments is not revealed by the supplier.

![Figure 4.12](image)

**Figure 4.12:** Absorption coefficients of PET based 3D printer filaments.

The absorption coefficient of three variants of PET 3D printer filament is shown in Fig. 4.12. All spectra are featureless in the THz regime, however interesting characteristics are observed between each filament. In the low frequency region below 0.6 THz, all the filaments are similar optically. Colorfabb-XT and PETG are identical with T-Glase showing a slightly elevated absorption. Differentiation between samples increases with higher frequency. Colorfabb-XT consistently remains the lowest absorbing material, T-Glase the strongest absorber with PETG ‘in the middle’. The absorption of PETG becomes comparable to T-Glase in the 0.9–1.3 THz
region before dropping lower again in the high frequency spectral region.

For THz optics, PETG and Colorfabb-XT become usable for frequencies lower than 0.62 THz reaching the threshold of 10 cm\(^{-1}\) for this region. In comparison, T-Glase does not reach this absorption limit until frequencies lower than 0.49 THz are present. The ideal absorption coefficient limit of 5 cm\(^{-1}\) is obtained for frequencies below 0.38 THz for PETG and Colorfabb-XT and is not reached for T-Glase in the observed spectral range. Thus, optically PET filaments are viable for THz optics up to 0.62 THz and suitable for quasi optics below 0.38 THz for PETG and Colorfabb-XT.

![Graph showing refractive index of PET based 3D printer filaments.](image)

**Figure 4.13:** Refractive index of PET based 3D printer filaments.

From Fig. 4.13 each filament shows a unique refractive index, reflective of the small composition changes between each filament. The refractive index of PETG filament is observed as 1.59 ± 0.01 across the spectrum, with Colorfabb-XT giving 1.64 ± 0.02 and T-Glase, 1.53 ± 0.01. T-Glase remains very consistent across the observed range, with PETG hinting at a very subtle decrease with higher frequency and Colorfabb-XT giving a slightly more significant decrease. The refractive index for PET is 1.48 in the visible spectrum [116]. This agrees with the THz data, as the filaments with refractive indices further from visible giving a stronger decrease across the THz region towards 1.48.
Overall printability of THz optics with PET is certainly feasible. The required hardware and user expertise required is comparable to ABS and other standard filaments. A heated bed is recommended but not necessary and should be kept below the glass transition temperature of 70 °C. This coupled with extrusion temperatures around 250 °C is well within the capabilities of most commercially available FDM printers. The optical properties are similar to ABS and not as desirable as HIPS but the visual transparency may provide advantages in some niche applications. For example, using PET as a window for an evacuated device would allow visible inspection of the device in operation.

4.2.8 High Impact Polystyrene

High impact polystyrene (HIPS), is a widely used FDM filament support material for dual extrusion printers. HIPS has a glass transition temperature of 100 °C and a thermal expansion coefficient of $80 \times 10^{-6} \text{°C}^{-1}$. With a glass transition temperature similar to ABS, extrusion temperatures the same as for ABS are permissible. Hence using HIPS alongside ABS in dual prints is a simple transition. Furthermore, HIPS will dissolve in a limonene bath. Consequently, HIPS is an ideal candidate as a structural support and internal material for ABS prints and is used primarily for this reason. Structural prints with this material are typically not a priority owing to inferior mechanical properties when compared to other filaments like ABS, nylon and PET. This include low tensile and flexural strength, low elastic modulus and elongation at break.

The absorption spectrum shown in Fig. 4.14 for HIPS gives some very encouraging results. The spectrum is featureless, increasing steadily with frequency. Pertinently this increase is significantly slower than with all other measured filaments. A useable frequency range up to 1.3 THz with absorption coefficient $< 10 \text{cm}^{-1}$ is observed. For frequencies below 0.88 THz the absorption coefficient drops below 5 cm$^{-1}$, with diffractive optics feasible in this region. The absorption coefficient further drops below 3 cm$^{-1}$ for frequencies less than 0.62 THz, corresponding to a
transmitted signal above 50% for 1cm bulk of material, which is a substantial result. The low frequency rise in absorption is an artefact of the experimental equipment.

**Figure 4.15:** Refractive index of high impact polystyrene 3D printer filament.

From Fig. 4.15 the refractive index of HIPS in the THz regime is given as $1.48 \pm 0.01$. This is observed to be highly consistent across the observed spectrum.
4.2.9 Polyvinyl Alcohol

Polyvinyl Alcohol (PVA), like HIPS, typically sees applications in FDM 3D printing as a support material with dual extrusion setups. The challenge with using PVA for this purpose is higher than HIPS, with PVA having differing thermal properties to ABS, as well as large water absorption. However, with care taken in filament storage and printer setup, successful prints are achievable [129]. Thermally, PVA melts at 104°C leading to an extrusion temperature of 190°C. With a thermal expansion coefficient of $70 \times 10^{-5} \text{C}^{-1}$, lower than most thermoplastics tested and comparable to PLA, warping of prints is minimal with PVA filament.

PVA filament is water soluble and cost effective, a combination which is unique to this filament, hence interest in its use as support and internal structure material. Also, due to PVA’s solubility, research is active in exploiting this characteristic and has lead to investigations in areas such as pharmaceuticals, where PVA is being used to print tablets that could be designed for tailored drug delivery to patients or to engineer specific drug release profiles [130].

![Absorption coefficient of polyvinyl alcohol 3D printer filament.](image)

**Figure 4.16:** Absorption coefficient of polyvinyl alcohol 3D printer filament.

From Fig. 4.16, a featureless absorption increasing steadily with frequency is observed. The absorption losses for PVA are significantly higher than other tested filaments across the spectrum. Even at low frequency, the absorption coefficient
is above $15\text{cm}^{-1}$, corresponding to $>97\%$ transmissive losses for 1 cm of material. Even thin printed optics will fail to be feasible with 1 mm of bulk still seeing $>30\%$ transmissive losses. Therefore, 3D printed devices tailored to THz applications are impracticable, if not impossible, with PVA filament.

![Figure 4.17: Refractive index of polyvinyl alcohol 3D printer filament.](image)
Fig. 4.17 shows the refractive index for PVA filament across the THz spectrum. This is observed to be $1.79 \pm 0.03$. Close inspection of the data hints a decrease of the refractive index with frequency. This is consistent with the visible refractive index of 1.5 for PVA.

Overall, despite the printability of PVA being quite beneficial, poor optical properties inhibit its use in 3D printing functional THz optics. To reach a useable threshold, optics would have to be kept to a millimetre or smaller in thickness. This is not only at the limit of the 3D printer but also beyond the capabilities of the PVA filament, being quite flexible and malleable. Across the entire spectrum, more suitable optical properties can be found from other filaments with PVA not showing any unique benefit pertaining to the THz regime. Even in its main commercial use as a support or internal dissolvable material, HIPS out-performs PVA. PVA can not be extruded at similar temperatures to other filaments because if it is kept above 200°C pyrolysis can occur which will jam the print mechanism, requiring drilling-out or replacement. The lower print temperature means adhesion between PVA supports and the print material becomes problematic. Test pieces in [129] showed a 50% success rate in printing a PVA block sandwiched between two slabs of ABS. Therefore PVA is superseded in all useable criteria for THz components and thus a poor choice for THz applications.

### 4.2.10 Conclusions

This chapter has evaluated the viability of standard commercially available 3D printer filaments and shown that optical properties are generally unaltered by mechanical modifications to these filaments. We conclude that ABS and HIPS filaments have the optimal compromise of a wide useable frequency range without too much complexity in achieving a successful print. Some of the best optical products are those that are most difficult to print: PP, PC, and PC/ABS Blend. Some nylon and PET modifications can fill niche applications because of their transparency in the visible spectrum. PVA printed devices are shown to be impracticable in the
THz region. A summary of the useable frequency range and printability is shown in table 4.2. Here the filaments are ordered according to their transmissive window, largest first. In the printability column easy filaments with three ticks correspond to those with low glass transition temperatures and thermal expansion coefficients, thus not requiring a heated print bed and minimal user expertise. Medium filaments with two ticks correspond to filaments that require a heated print bed to navigate a higher thermal expansion coefficient. Hard filaments with one tick are filaments with high glass transition temperatures and thermal expansion. These require parameters beyond the capability of most filament 3D printers and a high degree of user experience. A summary of the absorption coefficients is shown in Fig. 4.18. Here a representative from each pigment grouping is displayed for direct comparison. The increase in absorption coefficient at low frequency is an artefact of the experimental system, at the limits of the THz source.

Table 4.2: Summary of 3D Printer Filaments in the THz Regime.

<table>
<thead>
<tr>
<th>Filament</th>
<th>Absorption Coefficient &lt;10 cm(^{-1})</th>
<th>Ref. Index</th>
<th>Printability</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIPS</td>
<td>0.1–1.30 THz</td>
<td>1.48 ± 0.01</td>
<td>✓✓✓ easy</td>
</tr>
<tr>
<td>PC</td>
<td>0.1–1.00 THz</td>
<td>1.49 ± 0.03</td>
<td>✓ hard</td>
</tr>
<tr>
<td>PC/ABS</td>
<td>0.1–0.80 THz</td>
<td>1.51 ± 0.01</td>
<td>✓ hard</td>
</tr>
<tr>
<td>ABS</td>
<td>0.1–0.75 THz</td>
<td>1.49 ± 0.01</td>
<td>✓ medium</td>
</tr>
<tr>
<td>PP</td>
<td>0.1–0.60 THz</td>
<td>1.48 ± 0.01</td>
<td>✓ hard</td>
</tr>
<tr>
<td>PET (+Mods.)</td>
<td>0.1–0.57 THz</td>
<td>1.53–1.64</td>
<td>✓✓ medium</td>
</tr>
<tr>
<td>PLA</td>
<td>0.1–0.50 THz</td>
<td>1.56 ± 0.02</td>
<td>✓✓✓ easy</td>
</tr>
<tr>
<td>PLA/PHA Blend</td>
<td>0.1–0.50 THz</td>
<td>1.64 ± 0.02</td>
<td>✓✓✓ easy</td>
</tr>
<tr>
<td>Nylon (+Mods.)</td>
<td>0.1–0.50 THz</td>
<td>1.61–1.75</td>
<td>✓✓ medium</td>
</tr>
<tr>
<td>PVA</td>
<td>0.1–0.30 THz</td>
<td>1.79 ± 0.03</td>
<td>✓✓ medium</td>
</tr>
</tbody>
</table>
Figure 4.18: Summary of absorption coefficients for 3D printer filaments in the THz regime.
CHAPTER 4. 3D PRINTING IN THE TERAHertz REGIME

4.3 3D Printed Terahertz Diffraction Gratings and Lenses

Work presented in this section corresponds to the published work in [55].

4.3.1 Theory

Regular grating

The geometry of the regular grating [131] is shown in Fig. 4.19.

(a)

(b)

Figure 4.19: Regular grating. The period of the structure is $d = 3$ mm. The height of each bar is $h = 1.05$ mm. The structure is supported by a thin base of thickness $b = 0.1$ mm. The overall width is $W = 31.5$ mm (10.5 periods) and the overall length is $L = 20$ mm. (a) Perspective view. (b) Side view.

The diffraction gratings were designed to operate at a frequency, $f$, of 0.2 THz, corresponding to a wavelength, $\lambda$, of 1.5 mm. The material chosen was PLA. Other filaments discussed previously were not used as they were unavailable at the time when this work was completed. Using THz-TDS (Z-Omega system), we determined the refractive index of PLA at $f = 0.2$ THz to be $n = 1.56$.

To obtain intensity in the first-order diffraction peak a period of $d = 2\lambda = 3$ mm was chosen. To suppress even orders of diffraction, the height of the rectangular bars was set at $h = \lambda/2(n - 1) = 1.05$ mm.

The diffraction grating structure was supported on a PLA base of $b = 0.1$ mm. The overall width, $W$, of the structure was 10.5 periods, or 31.5 mm; the overall length, $L$, was 20 mm.
Scalar diffraction theory gives the transmission of the regular grating to be [132]:

\[
f(x) = \left\{ \left[ \text{rect}\left(\frac{2x}{d}\right) \otimes \delta(x) \right] + \left[ \text{rect}\left(\frac{2x}{d}\right) \otimes \delta(x - d/2) \right] \exp(i\phi) \right\} \otimes \text{comb}\left(\frac{x}{d}\right). \tag{4.1}
\]

Here \(x\) is the distance from the origin along the grating (the first “step” in the grating is centred at \(x = 0\)) and \(\phi\) is the phase difference. The phase difference is given by \(\phi = (2\pi h/\lambda)(n - 1)\).

**Blazed grating**

The geometry of the blazed grating is shown in Fig. 4.20.

(a) 

(b)

**Figure 4.20**: Blazed grating. The period of the structure is \(d = 3\) mm. The height of each wedge is \(h = 2.1\) mm. The structure is supported by a thin base of thickness \(b = 0.1\) mm. The overall width is \(W = 30\) mm (10 periods) and the overall length is \(L = 20\) mm. (a) Perspective view. (b) Side view.

As with the regular grating, to obtain intensity in the first-order diffraction peak, a period of \(d = 2\lambda = 3\) mm was chosen for the blazed grating. In the case of the blazed grating, to suppress the even orders of diffraction, the height of the grating was set at \(h = \lambda/(n - 1) = 2.1\) mm, twice as high as the regular grating. Again as with the regular grating, the blazed grating structure was built on a base of \(b = 0.1\) mm of PLA. The overall width, \(W\), was 10 periods (30 mm) and the overall length, \(L\), was 20 mm.
The blazed grating equation is:

\[ f(x) = \text{comb}(\frac{x}{d}) \otimes \text{rect}(\frac{x}{d}) \exp\left(\frac{i\phi x}{d}\right). \]  

(4.2)

As before, \( x \) is the distance from the origin along the grating, \( d \) is the period of the grating, and \( \phi \) is the phase difference, again given by \( (2\pi h/\lambda)(n-1) \). The blaze has a gradient of \( \phi/d \).

### 4.3.2 Experiment

The gratings were produced using an Ultimaker Original 3D printer utilising fused deposition modelling with a nozzle diameter of 0.4 mm. This setup prints with 2.85 mm PLA filament. Gratings were made with the following print specifications: layer height 0.01 mm, shell thickness 0.1 mm, print speed 50 mm/s, and print temperature 220°C. Owing to the need of a higher quality print, lenses were produced by MultiJet Modelling using a ProJet HD3500 plus 3D printer, using a proprietary photo-curable resin sold as Visijet Crystal. Multijet technology works via the use of an inkjet printhead. This lays a thin strand of the photo-curable resin, which is in turn solidified with a UV lamp. This gives a much higher resolution and smoother print unavailable with filament 3D printers.

Both the gratings and lenses are mechanically robust. Although the base of the gratings is thin (0.1 mm), they do not easily bend or break and are substantially stronger than other commonly used optical components such as beamsplitters and pellicles.

The experimental setup for measuring the diffraction gratings is shown in Fig. 4.21. In the setup, an adaptation is made to the two colour system discussed in chapter 3.0.1. The THz beam is first collimated and then focused onto the grating using two off axis gold plated parabolic mirrors. Parabolic mirrors used to collect transmitted radiation are replaced by a specifically engineered rotation stage. A metal arm, keeping a fixed distance of 100 mm from the diffraction grating permits the
CHAPTER 4. 3D PRINTING IN THE TERAHertz REGIME

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Figure 4.21: Experimental setup used in measuring PLA diffraction gratings.

detector to rotate through an angle \( \theta \) relative to the grating normal. A He-cooled Si bolometer, employed for photodetection, is mounted to the rotation arm via a specifically designed plate. This further ensures a consistent height is maintained between the photomixer, grating and bolometer window. In this configuration the minimal rotation angle measurable is 0.5 degrees. The frequency of the THz source was fixed at 0.2THz. The photomixer bias is modulated from 0-20 V at 183 Hz for lock-in detection. Measurements of the transmitted intensity were taken at angular increments of 1 degree with a 1 second integration time through a total range of \( \theta = \pm 90 \) degrees.

For the lenses, the focal length was measured by moving the lens along the optic axis relative to the detector, along the collimated THz beam.
4.3.3 Results

Transmission in the THz regime

The absorption coefficients of PLA and VisiJet are shown in Fig. 4.22. In common with many organic materials, the transmission is very good in the sub-THz range, then decreases with frequency. There is no clear cut-off in the frequency below which the materials may be used. If 0.1 transmission at 1 mm thickness is taken as the criterion, both materials are useful to about 0.7 THz. Other plastics have superior transmission in this range as discussed earlier in this chapter in section 4.2.

The results presented hereafter are all at frequency $f = 0.2$ THz. We designed the gratings as phase gratings but, in view of the non-negligible absorption, they will behave to some extent as amplitude gratings as well.
Gratings

The data pertaining to the regular grating appear in Fig. 4.23. Also shown in the figure is the expected behaviour as calculated from Eq. (4.1). It is seen that good agreement is obtained. In theory, there should be no transmission in the straight-through direction ($\theta = 0$), and equal peaks at $\theta = \pm 30$ degrees. While there is some leakage through the fabricated grating at $\theta = 0$, the equal peaks at $\theta = \pm 30$ degrees are apparent in the experimental data. The side lobes that are evident in the theory are hinted at in the experimental data by shoulders on the main peaks but the solid angle subtended by the detector is too large for these to be clearly resolved in the present experimental setup.

The data pertaining to the blazed grating appear in Fig. 4.24. Also shown in the figure is the expected behaviour as calculated from Eq. (4.2). It is seen that good agreement is obtained. It is expected that diffraction peaks will occur at $\theta = -30$ degrees, $\theta = 0$ degrees, and $\theta = +30$ degrees, which is borne out by experiment. The ratios of intensity are measured to be $60 \pm 1 : 28 \pm 1 : 12 \pm 1$, again
Figure 4.24: Blazed grating. Full circles—experiment. Full line—theory. The intensity is relative to the intensity when there is no grating in the beam.

close to the values as expected theoretically.

A numerical comparison between the experiment and theory is given in Table 4.3 for both the regular and the blazed grating.

Lenses

Preliminary measurements have also been made on 3D-printed lenses. The three lens designs chosen are illustrated in Fig. 4.25. They are symmetric, elliptical-aspheric, and planar-hyperbolic [51].

For each of the fabricated lenses, the focal length was measured to be $35 \pm 2$ mm. This is consistent with the calculated focal lengths, taking into account the cone angle and radial distance from the optical axis [51]. However, the absorption in these relatively thick optical elements has prevented more thorough optical characterization. Thinner lens designs and equivalent Fresnel lenses are the goal of ongoing work.
Table 4.3: Key characteristics of 3D printed gratings—theory and experiment.

<table>
<thead>
<tr>
<th>Order</th>
<th>( m = 0 )</th>
<th>( m = +1 )</th>
<th>( m = -1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regular grating</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Position (degrees)</td>
<td>—theory 0 +30 −30</td>
<td>—experiment 0 ± 0.5 +30 ± 0.1 −30 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Intensity (%)</td>
<td>—theory 0 46 46</td>
<td>—experiment 12 ± 1 45 ± 1 43 ± 1</td>
<td></td>
</tr>
<tr>
<td><strong>Blazed grating</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Position (degrees)</td>
<td>—theory 0 +30 −30</td>
<td>—experiment 0 ± 0.1 +30 ± 0.1 −30 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Intensity (%)</td>
<td>—theory 35 60 5</td>
<td>—experiment 28 ± 1 60 ± 1 12 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.25: Aspherical lenses fabricated by 3D printing (a) Symmetric, (b) Elliptical-aspheric, (c) Planar-hyperbolic.
4.3.4 Conclusions

In conclusion, it has been demonstrated that 3D printing techniques are effective for the fabrication of complex optical structures in the THz domain. This is a significant result as 3D printing offers a method for low cost, versatile, and fast fabrication. A blazed and regular grating design optimised for diffraction at 0.2 THz were considered with the diffraction patterns measured at a distance of 100 mm. The results, when compared to theoretically determined angular dependence, showed good agreement. Often the limitations of resolution and usable materials in 3D printing are a disadvantage for a wide range of fabrication applications. Our results establish that at THz frequencies the optical properties of the printable materials are favourable, at least for thin layers at low frequencies, and that the printable resolution is fine enough for the wavelengths of interest.
4.4 3D Printed Hollow-Core Terahertz Optical Waveguides With Hyperuniform Disordered Dielectric Reflectors

Work for this section was completed in collaboration with Tian Ma, Martin Girard, Maksim Skorobogatiy and Hichem Guerboukha from École Polytechnique de Montréal in Quebec, Canada. Reference [63] refers to the publication of this work. This section will focus on my contribution to the publication, centred on developing a 3D print design process for the hyperuniform waveguide. Detail of the experimental data and performance of the waveguide can be found in the aforementioned paper.

4.4.1 Introduction

In recent years, photonic crystals (PC) have developed a large amount of interest owing to their capabilities in manipulating light. These are developed naturally or artificially via periodic modulation of the refractive index or permittivity [133]. This modulation can be constrained to one dimension or developed across two and three dimensions depending on the desired application. Interestingly, observed phenomena are highly analogous to condensed matter. The modulating refractive index produces a lattice similar to an atomic lattice. Here photon interactions in the PC imitate electron-hole characteristics in the atomic lattice. This allows similar theoretical and computational techniques to be applied across both fields [133].

3D printing stands as an effective tool for developing PC devices, with refractive index modulation achieved via printable dielectric materials.

For this research a PC waveguide was 3D printed. The waveguide consists of a hollow core, with cladding made from dielectric cylinders connected with thin dielectric bridges, as shown in Fig. 4.27. The hyperuniform pattern of the dielectric cladding is governed by a metric, $\chi$, which generates a point pattern in k-space corresponding to the locations of the dielectric cylinders. A value of $\chi = 0$ gives
a random pattern from a poisson distribution, $\chi > 0$ will be disordered, while $\chi = 1$ will generate a crystal pattern [63]. A value of $\chi = 0.5$ was chosen for this waveguide as this design produces large photonic band gaps with better confinement than waveguides based on purely periodical PCs. 3D printing of this structure had already been attempted in [134] with standard ABS fused filament printing on a Makerbot Replicator 2X. These were unsuccessful with structures well below the resolution limit of this printer, shown in Fig. 4.26. Attempting to etch the models with acetone to thin out structures was also unsuccessful as this process compromised the structural integrity of the plastic in its entirety, as opposed to removing outer layers.

Figure 4.26: Attempted print in ABS showing clear failure with guiding region structures well below the resolution of the 3D printing process. Taken from [134].

### 4.4.2 Developing a 3D Printable Model

Fig. 4.27 shows a 2D top down view of the desirable geometry to be 3D printed. With $\chi = 0.5$, a honeycomb structure is generated in real space. In optimising the bandgap size a geometry of $\sim 100 \mu m$ diameter for the cylindrical rods and $\sim 30 \mu m$ dielectric bridges was chosen. A total guide length of 100 mm was required, with
this split up into $4 \times 25 \text{mm}$ sections, allowing cutback measurements in a THz-TDS setup.

Figure 4.27: Hollow core hyperuniform waveguide structure proposed for 3D printing.

These geometries are beyond the capabilities of any commercial resin/plastic 3D printer. This ideal structure was attempted to be printed on a top of the line printer: a Projet HD3500 Plus Multijet 3D printer. The prints immediately failed. The highest resolution of this printer is in the locale of the detail required for the waveguide, with a quoted xy precision of 25–50 $\mu$m dependent on the print geometry. While this indicates the printer can handle these features, this does not translate into real world precision across all applications. The geometry of the waveguide is very difficult to print. This is centred on the thin bridges. Producing such a thin, stand-alone object layer by layer is a strenuous task for any 3D printer, hence this was the determining factor in the failed print. The cylindrical posts are also quite onerous to print, however given the circular cross section and larger diameter, each successive layer consists a much larger platform to build off. Thus, these will not limit successful prints beyond the bridges.
In order to print such a delicate geometry, it was determined that the internal structure of the honeycomb must be modified. This is not ideal as altering the geometric properties of the waveguide cladding will reduce the photonic band gap. As such, adjusting the model needed to be kept to a minimum. In order to ascertain the limiting print resolution for this geometry, a test model was produced, shown in Fig. 4.28.

![Test print used to determine minimal geometries showing (a) top view and (b) side view.](image)

The test model was designed with the following considerations. The cylindrical sections were developed with a diameter of 100 µm, consistent with the smallest original geometry. This was kept fixed in keeping with the assertion that the thin bridges are the main variable in limiting the print resolution. A set of isolated cylinders were connected by thin bridges of varying thickness from 40 µm to 180 µm in 20 µm steps. The bridges were made to be 1 mm in length connected to opposing cylinders. This coincided with the length of the longest bridge found in the original design. Thus, a minimal cylinder diameter with the longest bridge present in the original design provided a suitable upper bound on the printer resolution. The cylinder face opposing the bridge connection was attached to a bulk section of 2 mm thickness. This isolated the cylinder-bridge connection as the only source of print
failure, ensuring the test design would not produce misleading information. An overall height of 5 mm was chosen, being a sufficient height to guarantee a successful geometry could be printed.

Results from the test print were very clear. Bridges with model thickness < 100 µm failed to print successfully. There was no gradual degradation as thickness was reduced, rather the bridge either passed or failed. Failed prints were observed to have a build up of resin near the cylinder but no connecting bridge from the first print layer. Successful prints showed a solid bridge with minimal defects. Thus it can be concluded that the window between a useable and unsuitable geometry is very narrow.

Consequently, a bridge thickness of 100 µm was chosen for the final print geometry. However, altering this on the original design still proved to be an arduous task. Modifications were made using AutoCAD 2015. The original waveguide geometry showing the connections between the dielectric bridges and cylinders as shown in Fig. 4.29

![Waveguide cladding showing the original geometric network of dielectric cylinders and bridges.](image)

**Figure 4.29:** Waveguide cladding showing the original geometric network of dielectric cylinders and bridges.

The bridges do not connect simply to cylindrical rods. Rather each rod com-
prises of its own specific geometry approximating a cylinder. These unique polygons vary in their size, number of faces and in their interface with subsequent bridges. This is especially apparent in the regions close to the hollow core, apparent in Fig. 4.29. Thus modifying the models to account for a larger bridge thickness is complicated. It was decided that the optimal process to achieve this would be to manually adjust the model geometry by hand as using modelling software introduced significant artefacts and unwanted alterations between the original and modified 3D model.

![Figure 4.30: Close up image showing connections between dielectric bridges and cylinders.](image)

Fig. 4.30 shows a close up of a typical connection between a series of bridges and a corresponding rod. From this figure, it can be seen that simply increasing the bridge width would result in sharp triangular sections at the intersection with each post. These must be smoothly joined to available points on the rod to ensure the printability of the model while minimising the impact of the modification on the overall waveguide structure.
Figs. 4.31 and 4.32 show the final modifications made to the 3D model in order to achieve a successful print. Each bridge is connected to the nearest available point on a relevant rod. Occasionally, this resulted in some bridges needing to be connected directly to an adjacent neighbour. However, it can be observed that this process has reduced the overall geometric alterations and hence minimise adverse
experimental outcomes.

### 4.4.3 Printing Process

Printed waveguide sections were performed on two different setups namely a 3D Systems Projet HD3500 plus and a Stratasys Objet350 Connex 3D printer. Both use a technology similar to stereolithography (SLA) 3D printers. The Connex prints via Polyjet (PJT) technology, while the Projet uses Multijet (MJT) technology. A standard SLA printer was also tested in printing the revised geometry, however a successful print was not possible. These systems all utilise a photo-curable resin and UV radiation. MJT is outlined in 4.3.2. PJT technology uses a thin layer of resin, which is cured by a precise beam of UV radiation. SLA machines utilise UV lasers which fire into a bath of resin, with the model drawn out of the resin overtime. This is in opposition to other methods built directly on a build plate.

The Projet HD3500 plus, according to specifications, was the best available printer hence the test print and model geometry were based on this printer’s capabilities. Prints performed on the Connex and SLA machine were performed for comparative purposes and to validate the experimental method in developing a printable waveguide.
Figure 4.33: Waveguide sections generated from 3D printing. (a), (c) and (e) were produced using multijet technology. (b), (d) and (f) were created using a stereolithography 3D printer. (e) and (f) show zoomed sections of the dielectric walls and corresponding connecting cylinder. Multijet printings shows a distinct advantage.

Fig. 4.33 illustrates the overall printed waveguide quality. It can be clearly seen that the MJT technology has outperformed the PJT. In Fig. 4.33 (a) and (b), the dielectric bridges and cylindrical rods are much more clearly defined in the MJT printed model. The bridges are also thinner and more accurate to the generated model. This is exemplified in the region of the hollow core. For the PJT print (b), many of the delicate structures have joined creating larger globular structures. Parts (e) and (f) further illustrate this point, with the MJT print distinct walls and connecting cylinders, while this is not apparent for the PJT technology. Resin is observed to be non uniform and suffering from many deformities, showing the
required resolution is beyond the printer’s capabilities. Despite the visual clarity and seemingly crisp detail, issues are still observed for the MJT print. Fig. 4.33 (e) shows an observed bridge thickness much larger than the proposed model. Overall the bridges are on average 200 µm, twice the insisted thickness. A region inside the bridges can be seen which is closer to the ideal, suggesting that resin has leaked/spread out during the print process. This is consequence of attempting to lay such a thin layer of photocurable resin at the limit of any 3D printer technology. It is hypothesised that the time delay in laying the resin before curing with UV radiation is the underlying cause of this issue. Fig. 4.33 (c) and (d) show the layer adhesion across the model. MJT printing (c) gives smooth consistent surfaces as the print is built up. PJT (d) does not match this, with resin from individual layers appearing to droop over previously printed layers. This seems to be a more exaggerated example of the resin not curing correctly resulting in distorted bridge thickness as explained previously. Brighter white sections observed in the images are remnants of support material and are not reflective of any abnormality.

In conclusion, the MJT printed waveguide can be considered successful. The bridge thickness is larger than desired, but the overall clarity and clear interface between the air and dielectric material has resulted in experimental data showing sufficient guidance and photonic band gaps, detailed in [63]. The increased printed thickness and altered geometry have served to reduce the overall capabilities of the hollow core waveguide. PJT printed waveguides are not considered successful. The lack of uniformity across the print resulted in too high scattering and disturbance to the photonic lattice resulting in no observed guidance for these samples.
Chapter 5

THz Spectroscopy Applied to the Analysis of Artists’ Materials

5.1 Introduction

Recent years have seen great success in applying THz techniques to the analysis of artists’ materials and in conservation science. This is outlined in chapter 2.5. This chapter will critically analyse a series of synthetic and natural pigments used by artists’, across industry and in culturally significant pieces. Namely, Quinacridone - a synthetic pigment giving red-violet shades, Phthalocyanine - a synthetic pigment showing blue-green shades, and a series of iron oxide ochres derived naturally and synthetically ranging through red, yellow, brown and black pigmentations.

5.2 Experimental Setups

5.2.1 Sample Preparation

Pigment samples were obtained across multiple suppliers. The precise pigment information and supplier details will be presented in the relevant introductory sections for each pigment class.

A commercial beeswax medium (R & F Handmade Paints [135]) was used to
bind the pigment powder into a paint. Beeswax was chosen as the medium since it exhibits low absorption losses across a large THz range (0–20 THz), as illustrated in Fig. 5.1. Here a sample thickness of a few millimetres still gives an absorbance less than 1. The detected transmission remained above 50% across the observed spectrum. With the equivalent of < 1 mm beeswax thickness used in measurements an adequate signal is guaranteed across the full spectrum accessible. A relatively large resonance at 6.4 THz must be noted and care taken to ensure this does not introduce unwanted artefacts in spectral analysis.

![Figure 5.1: Relative absorbance of white beeswax medium from 0.4–20 THz.](image)

White beeswax is decolorised by mechanical filtration, not chemical bleaching. This is important as chemicals used in bleaching other wax mediums react with some pigments. The melting point of 62–66°C is well below the temperatures required to cause phase or composition changes in any of the studied pigments. Thus, the pigment properties are not changed by the thermal or chemical processes employed in combining with white beeswax. Samples were made by mixing 0.7 g of melted beeswax with 0.07 g of paint pigment. This ratio (10:1) generates strong absorption features in the terahertz spectrum without sacrificing cut-off frequency. The molten mixture was cooled on perspex before being rolled to approximately 1 mm thickness.

As outlined in Section 4.2.1 consistency across sample preparation and measure-
ment procedures is important to draw accurate comparisons and conclusions from experimental results. As such, sample preparation and instrument settings outlined hereafter, were strictly adhered to ensuring the desired consistency.

5.2.2 Terahertz Spectroscopy

THz spectra were obtained from the following spectroscopic systems discussed in chapter 3: The Z-Omega Z2 THz-TDS in 3.1.1 (0.1–2 THz), the Advantest TAS7400TS THz-TDS in 3.1.2 (0.5–5 THz), the Bomem FTIR spectrometer in 3.2.1 (1–10 THz) and the Bruker IFS 125/HR Fourier Transform Spectrometer (2–12 THz) coupled to the infrared beamline at the Australian Synchrotron in 3.2.2. Each system fills a unique niche in understanding the THz response of desired pigments. The Advantest and Bomem spectrometers were utilised for initial low and high frequency measurements, while the Z-Omega Z2 and the Australian Synchrotron’s infrared beamline were employed for corresponding temperature dependence measurements.

For spectra taken on the Z-Omega system (3.1.1) the moving retroreflector was set to scan continuously at 0.01 mm/s. A total scan length of 10 mm was chosen giving a theoretical resolution limit of 15 GHz. With lock-in detection, a time constant of 300 ms was used. The system enclosure was purged with dry air to eliminate water absorption features. Purging times for a known gas pressure for this system are well understood and, in conjunction with humidity sensors, were used to ensure a suitably dry environment before data collection was commenced.

With the Advantest TAS7400TS system, THz spectra were generated using standard source/detector equipment as detailed in 3.1.2. The final spectrum was calculated as an average of 16384 rapid scans, chosen as a sufficient number to meet the criteria of minimising noise while remaining time efficient. The nominal resolution of 1.9 GHz was used for these measurements. The ‘optical board’ section of the apparatus was purged with dry air to eliminate water absorptions. This was ensured with humidity sensors placed throughout the system. All spectral measurements were made at a room temperature of 21°C.
In extending the spectral range to higher frequencies, the Bomem FTIR system (3.2.1) with the following parameters was used: A spectral range of 1–10 THz at an unapodized resolution of 0.03 THz. A helium cooled Si: bolometer was employed as the detector. Water vapour was removed by evacuating the system and guaranteed by waiting sufficiently for a low pressure to be reached.

With the Bruker/synchrotron setup (3.2.2) a 6mm multilayer mylar beamsplitter was employed resulting in an available 1–20 THz spectral range. Appropriate to this range, a helium cooled Si: Bolometer was used for photodetection. For spectral acquisition, 100 rapid scans were averaged with a 0.06 THz resolution. A dry sample and equipment environment was maintained by keeping the entire system under a high vacuum.

**Temperature Dependence**

For low frequency measurements made on the Z-Omega Z2 TDS system, cooling was achieved using a Janis CCS-350R closed cycle refrigerator, allowing sample temperatures down to 10 K. In taking spectra, the cold head of the refrigerator was suspended vertically into a Z-Omega Z2-TDS system as shown in Fig. 5.2.

![Figure 5.2: Z-Omega TDS experimental setup used for temperature dependence measurements.](image-url)
Pigment samples were mounted to the refrigerator cold head via copper plates serving as apertures with a 1 cm radius. Vacuum grease was used away from the aperture to stick the samples to the plate, aiding thermal conduction. Temperature measurements were made systematically from a temperature of 12 K through to 300 K; 25 K steps were deemed sufficient in monitoring the temperature dependence of spectral features. With each step a 30 min settling time was allowed before taking a spectrum. This ensured thermal equilibrium was reached between the sample and cold head interface. In regards to measurements at the Australian Synchrotron, cooling was achieved via a Cryo Industries closed cycle refrigerator system. This setup is coupled directly to the Bruker spectrometer. Samples were mounted onto copper plates with a 2 mm diameter aperture, which in turn were screwed directly to the cold head of the cryostat. Temperatures down to 6 K were reached with measurements made in 20 K steps up to 300 K. At each temperature, a minimum wait time of 10 mins was allowed to ensure thermal equilibrium between the sample, temperature sensor and cold head. In both systems the cold head is warmed via a thin resistive wire, externally regulated with standard PID controls.

Temperature measurements made at the Australian Synchrotron were in accordance with section 3.2.2. It should be noted that for some samples in the high frequency region of the Synchrotron source, the noise floor was reached. This appears as a noisy ‘capping’ in the THz absorbance spectrum. As this does not effect every pigment the full range will be given to show direct comparison between samples. Caution must be taken in interpreting any features centered on, or near, any of these regions where the noise floor is reached. As such, analysis will be intentionally withdrawn here.
5.3 Quinacridone Pigments

Work presented in this section is an amalgamation of two published works, which can be found in references [136, 137]. Solid State DFT calculations were performed by our collaborators: J. A. Zaczek and T. M. Korter.

5.3.1 Introduction and Theory

Quinacridone (QA), Fig. 5.3, discovered in 1935, has now become the most important pigment for red-violet shades, and is widely used in coatings, dyes, plastics, and printing inks, being light-fast, heat-resistant, and weather-resistant [138, 139]. Four crystalline phases are known: $\alpha^I$, $\alpha^{II}$, $\beta$, and $\gamma$ [140]. Since the $\alpha$ phases are thermodynamically unstable and not light-fast these do not find commercial application. On the other hand, the $\beta$ and $\gamma$ phases are rather stable and do not interconvert post-production, except in the presence of high temperatures and strong solvents such as concentrated NaOH. [140] Furthermore, doping the base structure,
typically with Cl or CH$_3$, broadens the range of shades available. An important example of doping is 2,9-dimethylquinacridone (2,9-DMQA; Fig. 5.4).

![Image of 2,9-dimethylquinacridone (2,9-DMQA).]

**Figure 5.4:** 2,9-dimethylquinacridone (2,9-DMQA).

The atomic structure of quinacridone is predominately planar benzene rings, with alternating nitrogen impurities opposing double bonded carbon and oxygen atoms (Fig. 5.3). In the $\beta$ phase each molecule is linked to its neighbours by two hydrogen bonds, each resulting in a series of long chains in the (110) and (110) directions. For $\gamma$ quinacridone a single molecule is linked to four neighbours via a single hydrogen bond. This gives rise to a ‘criss-cross’ [140] pattern rather different from the chains present in the $\beta$ phase. The resulting strong differences in the crystal packing between the crystalline phases subsequently leads to the distinct visible optical properties between each phase.

At least ten variations of ‘quinacridone’ pigments are commercially produced, including Pigment Orange (PO48, PO49), Pigment Red (PR122, PR192, PR202, PR206, PR207, PR209), and Pigment Violet (PV19, PV42) [141, 142]. This study will focus on three pigments, namely PR122 and two variants of PV19.

Confusingly, there is considerable discrepancy in the literature and among art suppliers in how different ‘quinacridones’ are described. To illustrate the variation in
CHAPTER 5. THZ SPECTROSCOPY OF ARTISTS’ MATERIALS

notation, let us begin with PR122. The label ‘PR’ stands for ‘Pigment Red’ (as indicated above). Accordingly, de Courlon et al. [143] describe PR122 as ‘quinacridone red’. Gottshaller et al. [144] likewise in one place (page 82) call PR122 ‘quinacridone red’ but in another place (page 88) call it ‘quinacridone magenta’. Lomax [145] calls PR122 ‘magenta yellow’ whereas Paulus et al. identify the colour as ‘more violet than gamma quinacridone’ [140]. In view of this confusion in descriptive nomenclature, this pigment will be refereed to simply as ‘PR122’. Labelling PV19 is not so simple. The difficulty here is that the label PV19 corresponds to pure quinacridone, but fails to specify the crystalline phase. The $\beta$ phase has a ‘reddish violet’ colour [140] and is called by art suppliers, such as Schmincke, [146] ‘quinacridone violet’. As such, this pigment will be referred to as ‘PV19-Violet’. On the other hand, the $\gamma$ phase is ‘red’ [140] and called by art suppliers, such as Langridge, [147] ‘quinacridone red’, hence this pigment will be referenced as ‘PV19-Red’.

Quinacridone pigments appeared commercially in the 1950s and are becoming increasingly important in works of modern art. For instance, the Italian painter Lucio Fontana is likely to have used quinacridone in the Pietre series (1951–1958) [144]. Likewise, the Australian painter Michael Johnson employed quinacridone in the fragile matt surface of the abstract work Night (1968) [143] as did Elizabeth Murray in Lu Lu Leaps (1995). The identification of quinacridone pigments in artworks is thus of practical and contemporary interest.

In analysing quinacridone pigments in a painting, the conventional tools of infrared or x-ray spectroscopy are of limited use. While near-infrared and mid-infrared spectroscopies may distinguish between different quinacridones, such photons do not penetrate far into the paint. Furthermore, while x-ray absorption and fluorescence are sensitive to average mass number and to particular atoms, respectively [148], they cannot distinguish different polymorphs. Although x-ray diffraction (XRD) can distinguish these, it is generally impractical for examining paintings. As Lomax concludes, “x-ray powder diffraction, therefore, is of limited utility in the identification of synthetic organic pigments in paints” [145]. In fact, quinacridone is given
as an exemplar in which the Rietveld refinement of the powder XRD data leads to a completely wrong structure [149]. Thus there is currently a need for better methods to investigate works of art and other cultural heritage items in determining the precise pigmentation.

This section will add powder x-ray diffraction (PXRD) analysis and solid-state density functional theory (ss-DFT) to terahertz spectroscopy to obtain a full understanding of the fundamental modes of three particular quinacridones: PV19-Violet, identified with $\beta$-QA; PV19-Red, identified with $\gamma$-QA; and PR122, identified with 2,9-DMQA.

Three commercial pigment powders were examined in this study. PV19-Violet, sold under the name ‘Quinacridone Violet’, was obtained from Schmincke [146]. PV19-Red, sold under the name ‘Quinacridone Red Pigment (Pigment Violet 19)’ was obtained from Langridge [147]. PR122, sold under the name ‘Quinacridone Magenta Pigment (Pigment Red 122)’, was also obtained from Langridge. (Additional PR122 pigment obtained from the art supplier Old Holland [150] was found to have an identical terahertz spectrum to the Langridge PR122).

5.3.2 Computational Methods

All ss-DFT simulations were performed using a developmental version of the CRYSTAL14 [151] software package. Structural optimisations were initiated with solid-state parameters based on the previously published x-ray data [140, 152]. The unit cell dimensions and atomic positions were allowed to fully relax within their respective space group symmetries. The Perdew-Burke-Ernzerhof (PBE) [153] exchange correlation functional and Ahlrich’s VTZ basis set was used with polarisation functions [154] added to all atoms. Truncation tolerances within the software used to describe the Coulomb and Hartree-Fock exchange integral series (keyword TOLIN-TEG) were set to $10^{-10}$, $10^{-10}$, $10^{-10}$, $10^{-10}$, and $10^{-20}$ hartree for all calculations. The calculations were augmented with Grimme’s DFT-D3 correction [155, 156] to better account for intermolecular London dispersion forces. An energy convergence
criterion of $\Delta E < 10^{-8}$ hartree was used in all geometry optimisations. Frequency analyses were performed on the final optimised structures to determine the vibrational frequencies and IR intensities (via the Berry phase method [157]) of the normal modes in these solids. For frequency simulations, the energy convergence was set to a more stringent $\Delta E < 10^{-10}$ hartree threshold.

5.3.3 Results and Discussion

Structural Analysis

Results of the structural calculation appear in Tables 5.1, 5.2 and 5.3, where they are compared to published single-crystal XRD data. The unit cells for the calculated structures of $\beta$-QA, $\gamma$-QA and 2,9-DMQA are depicted in Figs. 5.5, 5.6, and 5.7, respectively.

Table 5.1: Comparison of the calculated and measured crystallographic unit cells for $\beta$-QA.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calc.</th>
<th>Exp.[140]</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$/Å</td>
<td>5.67</td>
<td>5.69</td>
<td>0.37</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>3.92</td>
<td>3.98</td>
<td>1.28</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>29.69</td>
<td>30.02</td>
<td>1.01</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>657.25</td>
<td>674.50</td>
<td>2.55</td>
</tr>
<tr>
<td>$\alpha$°</td>
<td>90</td>
<td>90</td>
<td>–</td>
</tr>
<tr>
<td>$\beta$°</td>
<td>95.84</td>
<td>96.76</td>
<td>0.95</td>
</tr>
<tr>
<td>$\gamma$°</td>
<td>90</td>
<td>90</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 5.2: Comparison of the calculated and measured crystallographic unit cells for $\gamma$-QA.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calc.</th>
<th>Exp.[152]</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$/Å</td>
<td>13.50</td>
<td>13.70</td>
<td>1.460</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>3.84</td>
<td>3.88</td>
<td>1.159</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>13.27</td>
<td>13.40</td>
<td>0.9701</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>679.81</td>
<td>700.63</td>
<td>2.969</td>
</tr>
<tr>
<td>$\alpha$°</td>
<td>90</td>
<td>90</td>
<td>–</td>
</tr>
<tr>
<td>$\beta$°</td>
<td>98.54</td>
<td>100.44</td>
<td>1.853</td>
</tr>
<tr>
<td>$\gamma$°</td>
<td>90</td>
<td>90</td>
<td>–</td>
</tr>
</tbody>
</table>

As shown in Table 5.1 and 5.3, the simulations of the solid-state structures match very well with the earlier experiments, but reveal a consistent underestimation of
Table 5.3: Comparison of the calculated and measured crystallographic unit cells for 2,9-DMQA.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calc.</th>
<th>Exp.[152]</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/Å</td>
<td>3.901</td>
<td>3.87</td>
<td>0.93</td>
</tr>
<tr>
<td>b/Å</td>
<td>6.304</td>
<td>6.37</td>
<td>1.07</td>
</tr>
<tr>
<td>c/Å</td>
<td>15.59</td>
<td>15.78</td>
<td>1.20</td>
</tr>
<tr>
<td>V/Å³</td>
<td>377.0</td>
<td>381.53</td>
<td>1.18</td>
</tr>
<tr>
<td>α/°</td>
<td>94.61</td>
<td>93.94</td>
<td>0.71</td>
</tr>
<tr>
<td>β/°</td>
<td>91.01</td>
<td>91.51</td>
<td>0.55</td>
</tr>
<tr>
<td>γ/°</td>
<td>99.91</td>
<td>100.00</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The approximately 3% volume contraction is not unusual for organic crystals over this temperature range, with a smaller contraction observed in 2,9-DMQA due to its colder experimental conditions.

Figure 5.5: Crystallographic unit cell of the calculated β-QA structure.
PXRD Comparison

PXRD measurements were undertaken to confirm sample purity and identity. Previous authors have presented PXRD graphs for quinacridones but without giving numerical data [140, 158]. We have digitised these previously reported spectra to compare with ours. In addition, comparison has been made between PXRD spectra and the ‘strong’, ‘medium’, and ‘weak’ reflections tabulated by Smith [159]. Finally, diffraction patterns have been calculated from the calculated structures, which are now presented with experimental PXRD data.

PXRD data is not unambiguous, as has been pointed out by Buchsbaum and
Schmidt [149]. Citing β-QA and γ-QA PXRD as examples, they demonstrated that a reasonable Reitveld refinement may lead to a completely wrong crystal structure (their emphasis). Thus caution is required in interpreting PXRD data.

Very good agreement is found between our PXRD data for the PV19-Red pigment and our calculations for γ-QA (Fig. 5.8). Moreover, all the lines tabulated previously are reproduced. [159].

We also see some additional smaller features that appear in the later reports [140, 158]. On this basis we are confident that the pigment we label PV19-Red comprises γ-QA.

Figure 5.8: Experimental PXRD of PV19-Red pigment and comparison with that of calculated γ-QA.

Quite good agreement is found between our PXRD data for PV19-Violet pigment and our calculation for β-QA (Fig. 5.9). We observe the features previously reported [140, 158, 159]. We also detect lines at about 12° (which may be an unresolved splitting) and 25° that are not evident in the other reported diffraction patterns [140, 158] or our calculation. These lines may indicate minor amounts of
an additional phase or phases.

Figure 5.9: Experimental PXRD of PV19-Violet pigment and comparison with that of calculated $\beta$-QA.

For PR122 we also obtain good agreement between our data, our calculations for 2,9-DMQA and the earlier tabulation of lines [159] (Fig. 5.10). On this basis we are confident to identify our PR122 pigment with the chemically-engineered variant 2,9-DMQA.
Figure 5.10: Experimental PXRD of PR122 pigment and calculation for 2,9-DMQA.

**Terahertz Spectroscopy**

Fig. 5.11 shows the transmissive properties of PV19-Red and PR122 (magenta) pigments from 0.5–4.5 THz. Generally, transmission in the sub-THz region is very high and observed to decline with higher photon energies to an eventual cutoff around 5 THz. This is characteristic of many organic substances in this regime. Overlaid on this gradual reduction in transmission, four or five strong resonances are observed across the spectrum. Furthermore, these absorptions show a clear shift between the two quinacridone pigments. Spectral features are labelled and summarised in Table 5.4.

These measurements were performed before PV19-Violet pigment had been obtained hence its omission in this section of the analysis. Later measurements, both theoretical and experimental show no interesting phenomena at these low frequencies for this pigment. As such PV19-Violet will be analysed in higher frequency
spectra presented in later sections.

**Figure 5.11:** Transmission spectra of PV19-Red and PR122 in the 0.5–4.5 THz range. Line colour denotes an exact representation of the pigments’ optical appearance. Magenta (RGB) - (168, 10, 68) - dashed, Red (RGB) - (251, 28, 59). RGB values are given for 0–255 range.

**Table 5.4:** Summary of room-temperature THz absorptions for quinacridone pigments.

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Position (THz)</th>
<th>Error (THz)</th>
<th>FWHM (THz)</th>
<th>Error (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV19-Red - 1</td>
<td>1.453 ± 0.023</td>
<td>0.30 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PV19-Red - 3</td>
<td>3.012 ± 0.009</td>
<td>0.32 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PV19-Red - 4</td>
<td>3.227 ± 0.006</td>
<td>0.16 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PV19-Red - 5</td>
<td>4.037 ± 0.002</td>
<td>0.28 ± 0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR122 - 1</td>
<td>1.742 ± 0.007</td>
<td>0.14 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR122 - 2</td>
<td>2.610 ± 0.021</td>
<td>0.50 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR122 - 3</td>
<td>3.167 ± 0.007</td>
<td>0.43 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR122 - 4</td>
<td>3.584 ± 0.013</td>
<td>0.45 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR122 - 5</td>
<td>4.384 ± 0.004</td>
<td>0.32 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Peaks 1, 3, 4 and 5 in PV19-Red appear to be similar to features 1, 2, 3 and 4 in PR122 only red shifted by 0.2–0.3 THz. This is consistent with literature, with Paulus et al. [140] asserting that doping the base quinacridone structure forces the crystal packing into the \( \gamma \) phase, i.e. the same phase as PV19-Red. The similar
THz spectral profile, reflects this notion, with added mass from the methyl groups believed to account for the lower frequency of each vibrational mode.

The experimental terahertz spectra are now presented and compared with the calculations. The calculations are presented as line spectra. In addition, for ease of comparison, the theoretical spectra have been convolved with Lorentzian line shapes with full-width half-maxima (FWHM) of 5 cm$^{-1}$ and these convolved spectra are also presented.

The PV19-Red pigment experimental spectrum shows very good agreement with the simulation for $\gamma$-QA. The main feature at around 9 THz and three very minor satellites are all evident in both experiment and simulation (Fig. 5.12). Likewise, the complex of half a dozen lines around 3 THz appears in both experiment and simulation. The only discrepancy is that a strong absorption predicted at about 4.5 THz is not evident in the experiment; this is related to an instrumental artefact, as it appears in all of the terahertz spectra. A strong window absorption with a simultaneous beeswax resonance prevents any signal at this frequency. Experiments presented in later sections using synchrotron radiation reveal this absorption and confirm its agreement with ss-DFT.

The PV19-Violet pigment experimental spectrum shows the features predicted by the $\beta$-QA simulation, namely, a strong absorption around 9 THz and a series of modes around 4 THz (Fig. 5.13). However, the experimental spectrum shows additional absorptions (notably at around 8.5 THz and 10.5 THz) not evident in the simulation. These additional absorption features we attribute to an unknown phase (or phases). This assessment is consistent with our PXRD investigation of this pigment.
The PR122 experimental and calculated spectra are in very good agreement (Fig. 5.14). There is a pair of modes between 10 and 11 THz, a second pair at around 7 THz, and a group of three around 3.5 THz.
Figure 5.13: Experimental terahertz spectrum of PV19-Violet pigment compared with the calculated spectrum for $\beta$-QA.
In all of the quinacridone solids, similar vibration types contribute to the observed THz spectra. These vibrations all correspond to intramolecular motions with the majority composed of wagging, rocking, and twisting of the quinacridone rings. The most intense THz spectral feature in all three samples is assigned to an in-plane rocking vibration of the carbonyl oxygens. The intermolecular vibrations (e.g. translations) of the molecules within these solids are IR-inactive and therefore play no role in the THz absorption profile.

**Temperature Dependence**

Fig. 5.16 and Fig. 5.15 show the temperature dependence of the lowest energy absorptions (Peak 1) for both \( \gamma \)-QA and 2,9-DMQA pigments. Both peaks show a marked temperature dependence with the magenta pigment (Fig. 5.16) seeing the peak shift from 1.50–1.59 THz and increase in amplitude by around one third. Sim-
Similarly, the red pigment peak (Fig. 5.15) also moves to higher energies, from 1.78–1.89 THz, hardening with an amplitude increase of about two thirds.

![Figure 5.15: Peak 1 position as a function of temperature for γ-QA.](image1)

Figure 5.15: Peak 1 position as a function of temperature for γ-QA.

![Figure 5.16: Peak 1 position as a function of temperature for 2,9-DMQA.](image2)

Figure 5.16: Peak 1 position as a function of temperature for 2,9-DMQA.

The peak shift to higher energies with lower temperatures is found to be linear in nature as can be seen in Fig. 5.18 and Fig. 5.17. From the linear fit present
in these figures, the peak positions (in THz), $P$, as a function of temperature (in kelvin), $T$, can be found analytically for each case: $P_\gamma(T) = 1.889 - 0.00036 \cdot T$ and $P_{DMQA}(T) = 1.588 - 0.00024 \cdot T$

In $\gamma$-QA the low energy resonance shifts significantly more than the corresponding peak in PR122 pigment, showing a larger slope in the linear fit.

**Figure 5.17:** Peak position as a function of temperature for $\gamma$-QA pigment. Raw data is given by the small crosses with a solid line representing a linear fit.

**Figure 5.18:** Peak position as a function of temperature for 2,9-DMQA pigment. Raw data is given by the small crosses with a solid line representing a linear fit.
Temperature Dependence with Synchrotron Radiation

Temperature measurements made at the Australian synchrotron are presented in Figs. 5.21, 5.19 and 5.22. These extend the cutoff frequency from 1.8–12 THz, allowing probing of the temperature response of all quinacridones THz features. Furthermore, the 4.5 THz region is better resolved in these spectra in comparison to the FTIR data. The strong 4.4 THz resonance lost in the window absorption presented in Fig. 5.12 for \( \gamma \)-QA is confirmed in the synchrotron data. Features across the spectrum show temperature dependence in all the quinacridones.

\[ \text{Figure 5.19: THz spectroscopy of } \gamma \text{-QA from 20 K–300 K with synchrotron radiation.} \]

\( \gamma \)-QA resonances generally show a blue shift of 0.1–0.2 THz and corresponding strengthening with cooling to 20 K. Of the 15 modelled peaks, there are two which do not follow this trend. Peak 12 (5.25) has a flat temperature response, with local shifts in amplitude smoothing out over the whole temperature range. This should be interpreted with caution as this peak is closely spaced to the large carbonyl oxygen resonance and splits out if this resonance at low temperature. This is reflected in the variability of the amplitude data. Peak 15 (5.26), a weak resonance at 9.9 THz, shows a tendency towards lower energies upon cooling. This is the only peak observed to soften at low temperature in \( \gamma \)-QA.
Low temperature measurement have revealed new closely spaced features more inline with DFT calculations presented previously. These are illustrated in 5.20. In (a), a single weak absorbance at room temperature splits into two distinctive peaks at 2.6 THz and 2.7 THz. This is in agreement with theory showing two closely spaced, weak absorbances in this region. (b) shows a new, non-temperature dependent feature at 8.9 THz for temperatures below 250 K. However this case presents a discrepancy with DFT calculations, which predict a single large absorption with three weak satellites in this region. These become more apparent in the temperature data, but the extra resonance is not expected, attributed to small impurities or unwanted phases present in the pigment sample.

Figure 5.20: New resonances resolved at low temperature in γ-QA.

Low temperature spectra for β-QA also enhance the agreement between experimental data DFT calculations. In the 4 THz region, closely spaced features unresolved at room temperature are evidenced in altering the temperature. Relative shifts between these vibrations with changing temperature are corroborated with ripples on the right shoulder of this absorbing region. At 20 K one of these intramolecular modes becomes fully resolved. A weak vibration predicted at 6.4 THz not seen at room temperature becomes visible with low temperature spectroscopy. Similarly two satellites are predicted by DFT in the region of the major 9 THz peak. Experimental data at 300 K shows no evidence of these minor features, however low temperature spectroscopy shows a small feature at 9.7 THz in conjunction with a
broadening of the low frequency shoulder of the main peak. These may account for the predicted modes.

\textbf{Figure 5.21:} THz spectroscopy of $\beta$-QA from 20 K–300 K with synchrotron radiation.

In the complex of resonances around 4 THz, two could be appropriately fitted and modelled (peaks 1 and 2 in 5.27). Both of these show a linear shift to higher energy with cooling until 100 K, below which both features plateau. Peak 1 shifts around 0.2 THz with a minor increase in amplitude while peak 2 shifts 0.25 THz, with its amplitude constant across the temperature range. The characteristic in plane rocking (peak 8) shows a smaller shift of 0.1 THz before also flattening below 100 K. This mode also strengthens from 1.4 at 300 K to 2 at 20 K.

Outside these main features, a range of temperature dependence characteristics are observed. Peaks 5, 10 and 12 follow the previous resonances in moving linearly with cooling to higher frequency before reaching a plateau below 100 K. In these cases the shifts in position are relatively smaller in the region of 0.1 THz. Interestingly, peaks 4, 13 and 14 soften slightly with cooling. This red shifting is clear but kept below 0.1 THz across the full temperature range. The position of peaks 3, 6, and 7 remain consistent with temperature changes. All resonances with an absolute amplitude greater than 0.5 are observed to strengthen at low temperature. Weaker resonances may show this characteristic, but difficulties in resolving these features at
higher temperatures stifle this analysis. Outside of peak 1, the amplitude doubles for all prominent features across the spectrum. Detailed illustration of these are given in Figs. 5.23, 5.24, 5.25 and 5.26. Peak 3 and 13 only become resolved below 200 K, while peak 6 is apparent only below 150 K hence data above these temperatures is omitted.

![Graph](image)

**Figure 5.22**: THz spectroscopy of 2,9-DMQA from 20 K–300 K with synchrotron radiation.

Fig. 5.22 gives temperature measurements for 2,9-DMQA. Vibrational modes presented previously are verified with low temperature measurements, in conjunction to more distinctly resolving some of the minor features predicted in DFT calculations. A small absorbance expected at 5 THz, not seen definitively at room temperature is resolved in cold measurements. A lobe observed in Bomem FTIR measurements on the high frequency side of the main 7.3 THz peak is not replicated in this data, suggesting this phenomena is not real and resultant of experimental artefact. Also, two small broad absorbing regions become present at 9.1 THz and 9.9 THz, below 200 K not present in DFT calculations. These are attributed to trace impurities in the sample, as reflected in PXRD analysis.

Generally, a blue shift with cooling is observed for spectral features. Only peak 11 is observed to not follow this trend exhibiting no positional dependence on temperature. The degree of peak hardening is similar for each mode, between
0.1–0.2 THz. The more prominent resonances further exhibit a strengthening for low temperatures. This exists for peaks with amplitudes above 0.5 at 300 K. Features below this amplitude are difficult to resolve, especially in the presence of thermal noise, thus finding reliable trends with temperature is unfeasible in these cases. Interestingly, many of the stronger peaks show dramatic alterations in their temperature profile at 150 K. Peak 3 shows no shift in amplitude before rising considerably below 150 K. Peak 6 strengthens steadily before a sharper rise at 150 K, subsequently flattening out below 100 K. Peak 7 strengthens linearly until 150 K at which point a plateau is reached. Full illustration of the positional and amplitude dependence of 2,9-DMQA can be found in Figs. 5.31, 5.32 and 5.33.
Figure 5.23: Temperature dependence of position and amplitude for vibrational modes in $\gamma$-QA from 2–3.5 THz.
Figure 5.24: Temperature dependence of position and amplitude for vibrational modes in \( \gamma \)-QA from 3.5–6.5 THz.
Figure 5.25: Temperature dependence of position and amplitude for vibrational modes in $\gamma$-QA from 6.5–9 THz.
Figure 5.26: Temperature dependence of position and amplitude for vibrational modes in $\gamma$-QA from 9–11 THz.
Figure 5.27: Temperature dependence of position and amplitude for vibrational modes in $\beta$-QA from 3–6 THz.
Figure 5.28: Temperature dependence of position and amplitude for vibrational modes in $\beta$-QA from 6–9 THz.
Figure 5.29: Temperature dependence of position and amplitude for vibrational modes in $\beta$-QA from 9–11 THz.
Figure 5.30: Temperature dependence of position and amplitude for vibrational modes in $\beta$-QA from 11–12 THz.
Figure 5.31: Temperature dependence of position and amplitude for vibrational modes in 2,9-DMQA from 3-6 THz.
Figure 5.32: Temperature dependence of position and amplitude for vibrational modes in 2,9-DMQA from 6–9.5 THz.
Figure 5.33: Temperature dependence of position and amplitude for vibrational modes in 2,9-DMQA from 9.5–11 THz.
Overall, low temperature spectroscopy reveals interesting insight into the understanding of the THz response of quinacridone pigments. The agreement between theoretical DFT calculations and experimental data is replicated and enhanced with low temperature spectroscopy. Previously unresolved theoretical peaks become apparent at low temperature, as does a clear distinction between some closely spaced, overlapping resonances. The intramolecular wagging, rocking and twisting motions of the quinacridone rings generally increase in frequency with low temperature. In γ-QA and its isomorphic variant 2,9-DMQA the hardening of features is consistent, in the region of 0.1–0.2 THz. For β-QA the differing crystal phase and resultant packing motif is reflected in the temperature analysis. Positional dependence is pointed more towards a lower energy shift with cooling. Features that harden with temperature only do so by less than 0.1 THz, and other resonances show softening with temperature, not seen in its polymorphic counterparts. The main characteristic feature, an in-plane rocking vibration of the carbonyl oxygens, observed in each pigment, shows a similar temperature response, also reflective of the presenting crystal phase. In γ-QA this is present at 9 THz with 2,9-DMQA giving this peak at 7.3 THz. Both show a linear hardening of the peak with cooling of 0.1 THz from 300 K to 20 K. Furthermore, both isomorphs give similar amplitude characteristics. A linear increase above 40% is found from 300 K to 150 K. At 150 K the amplitude remains constant for lower temperatures in both cases. For β-QA the positional dependence is consistent however, the amplitude increases until 75 K before seeming to level out for lower temperatures.
5.3.4 Conclusions

It has been shown, by experiment and simulation, that the characteristic vibrational modes of $\beta$-quinacridone, $\gamma$-quinacridone, and 2,9-dimethylquinacridone all fall in the terahertz spectral range and all have similar origins in fundamental wagging, twisting, and rocking motions. Furthermore, in spite of these similarities, it has been demonstrated that the terahertz spectra of three quinacridones differ sufficiently to unambiguously distinguish the three quinacridones. These findings invite the application of terahertz spectroscopy in the dating and authentication of works of art.

In particular, it has been demonstrated that terahertz spectroscopy identifies characteristic ‘fingerprints’ of three commercial quinacridone pigments. A distinct advantage of terahertz spectroscopy is its use as a non-destructive tool for penetration into hidden regions or pentimenti of an art piece to yield chemically specific information. This capability of terahertz-frequency photons gives advantages over visible, infrared and x-ray electromagnetic radiation in examining artwork. Of course, most art is produced with the aim that it is to be viewed by the human eye in the visible spectral region. Yet many different pigments appear to have the same colour to the human eye. Terahertz spectroscopy is able to distinguish these. Secondly, terahertz photons penetrate deeper into material, and so can probe the paint further below the surface, than near- or mid-infrared photons. Thirdly, although x-ray absorption and fluorescence are sensitive to average mass number or to particular atoms, respectively, they cannot distinguish different polymorphs, such as $\beta$- and $\gamma$-quinacridone. Thus, terahertz methods have important advantages over visible, infrared and x-ray methods. Art fraud, for example, might be detected, if a painting claimed to be pre-modern was found to contain synthetic quinacridone pigments, since quinacridone was first synthesised in 1935.
5.4 Phthalocyanine Pigments

5.4.1 Introduction/Theory

Phthalocyanine (Fig. 5.34) is a porphyrin chemical compound used in an array of applications including pigments, dyes and semiconductors. The base structure permits a large number of elemental doping sites on the outer benzene structures, with accepted notation shown in Fig. 5.34. Furthermore, the central porphin structure allows the inclusion of metal elements leading to a large range of metal-phthalocyanine derivatives, each with unique and intriguing characteristics. One such example, Copper-Phthalocyanine (CuPc) depicted in Fig. 5.35, is widely used as a synthetic pigment.

CuPc was first produced commercially in 1935. Since its inception, CuPc has become the most widely used and important synthetic pigment. CuPc exhibits incredible light and weather fastness, superior to any other organic pigment [159].
CuPc is polymorphic, with five current crystal phases known. These are given descriptors $\alpha, \beta, \gamma, \delta$ and $\epsilon$. The planar porphyrin structure of CuPc results in a macromolecular structure of these planes linearly stacked on top of each other, similar to a ‘stack of coins’ [162]. The various polymorphs only differ in the relative orientation of successive stacks. Of the aforementioned five modifications, three see commercial use as pigments. These are the $\alpha, \beta$ and $\epsilon$ phases.

CuPc is generally sold under the proprietary name ‘Phthalocyanine Blue’, which can contain one or many of the CuPc crystal phases. As a pure pigment, six variations are sold under the colour index (C.I.) name of PB15. These are outlined in Table 5.5.

Table 5.5: Comparison of CuPc pigment phase and characteristics.

<table>
<thead>
<tr>
<th>C. I. Name</th>
<th>Crystal Phase</th>
<th>Properties</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB15</td>
<td>$\alpha$</td>
<td>unstabilised</td>
<td>reddish blue</td>
</tr>
<tr>
<td>PB15:1</td>
<td>$\alpha$</td>
<td>phase stabilised</td>
<td>reddish blue</td>
</tr>
<tr>
<td>PB15:2</td>
<td>$\alpha$</td>
<td>phase/ flocculation stabilised</td>
<td>reddish blue</td>
</tr>
<tr>
<td>PB15:3</td>
<td>$\beta$</td>
<td>unstabilised</td>
<td>greenish blue</td>
</tr>
<tr>
<td>PB15:4</td>
<td>$\beta$</td>
<td>flocculation stabilised</td>
<td>greenish blue</td>
</tr>
<tr>
<td>PB15:6</td>
<td>$\epsilon$</td>
<td>unstabilised</td>
<td>reddish blue</td>
</tr>
</tbody>
</table>
From Table 5.5, CuPc generates blue shades of pigment dependent on the presenting phase. The $\alpha$ phases give a reddish shade of blue, while this extends into greener shades of blue for the $\beta$ phase. $\alpha$-CuPc is unstable and can inter-convert post production in industrial environments. The stabilised versions PB15:2/3 are achieved by doping the outer rings with 4–5 Cl atoms, which gives these pigments a slightly greener tinge [161]. The $\beta$ phase is highly stable. The $\epsilon$ phase, exhibiting a strong reddish blue colour is largely unstable. Stabilised versions of this pigment show a greener shade, attributed to some $\epsilon$-CuPc interconverting to $\beta$-CuPc.

The available colours of CuPc pigments can be further extended with halogenation of the outer benzene rings. This is typically achieved with Cl and Br atoms. Chlorinated CuPc (Cl-CuPc), Fig. 5.36, alters the pigment colour to green when 14–15 Cl sites are present on each CuPc molecule. This is sold as Pigment Green 7 (PG 7). Cl-CuPc is isomorphic to $\alpha$-CuPc, with no other crystalline phases reported.

Pigment Green 36 (PG36) is another halogenated example of CuPc. In this case up to 12 of the Cl atoms in Cl-CuPc are replaced with Br atoms. This takes the green pigment colour into more yellow shades. The degree of the shift to yellow
shades is directly proportional to the Br content. As with Cl-CuPc, this variant only shows a single crystal phase [161].

In this study, the THz response of two variants of CuPc pigments are investigated. These are the standard $\beta$ phase (PG15:3) as well as the chlorinated variant (PG7). These were obtained from Langridge [147] sold under the proprietary names of phthalo blue and phthalo green respectively. No indication is offered by the supplier pertaining to the purity of each samples phase and composition. Thus care must be taken in attributing spectral features directly to a specific phthalocyanine crystal phase.

5.4.2 Results and Discussion

PXRD

Experimental PXRD data for phthalo blue and green pigments are displayed in Figs. 5.37 and 5.38. These were partaken to ensure sample purity, identification and draw connections between the pigment classification and presenting crystal phase. Data pertaining to both pigments is definitive. Analysis was performed using Traces 6.6.10 software and corresponding database. Tabulated data is also present for PB15:1, PB15:3 and PB6 (labelled PB epsilon) in [159].

Fig. 5.37 shows experimental data consistent with $\beta$-CuPc, obtained from the traces database. Tabulated data by Smith [159], for PB15:3 is also in agreement with all reported peaks reproduced in the experimental data. Coupled with the assertion from Kadish [161], that the $\beta$ phase of CuPc is highly stable and the only constituent of PB15:3, strong confidence is realised that the tested sample is pure PB15:3, which in turn is $\beta$-CuPc. Data was further contrasted with XRD patterns for PB15:1 ($\alpha$-CuPc), PB15:4 (flocculation stabilised $\beta$-CuPc) and PB6 ($\epsilon$-CuPc). XRD peaks in these cases are clearly distinguishable from PB15:3, with no features consistent with the presented data. Thus no cross contamination is present.

PXRD data for phthalo green is consistent with Traces database data for C. I. Pigment Green 7. Diffraction intensities are somewhat lower across the scanned
Figure 5.37: Experimental PXRD of phthalocyanine blue pigment in comparison with $\beta$-CuPc.

Figure 5.38: Experimental PXRD of phthalocyanine green pigment in comparison with PG7.

range, however all peaks are present and correctly located. Further complementary data is scarce in comparison to phthalo blue. Despite this, it is clear the sample
consists of PG7, with no evidence of contamination with other materials. Kadish, Smith and Dahlen [159, 161, 163] all support the case that the sample comprises Cl-CuPc in its entirety. No alternate phases are possible and no external additions are made to this pigment.

**Terahertz Spectroscopy**

THz spectra were taken across a full range extending from 0.05–20 THz. Data obtained in the 0.05–2 THz region on the Z-Omega system were featureless and give no useful insight, hence are omitted from this analysis.

![Absorption spectra of phthalo blue and green](image)

**Figure 5.39:** Absorption spectra of phthalo blue and green from 0–5 THz.

The low frequency THz response of phthalo blue and green pigments is given in Fig. 5.39. For the blue variant two large resonances at 3.72 THz and 4.6 THz are present. In contrast, phthalo green is featureless across the spectrum. As with visible photons, THz photons are also sensitive to the macromolecular changes intrinsic to these pigments. Experimental data presented is consistent with Fukunaga [88] over a similar spectral range. Unfortunately, no mention is made to the specific pigment used or crystal phase in this case.

Extending the observed spectrum to 20 THz using a synchrotron source reveals a series of spectral features in both pigments. Phthalo blue consists of a series of sharp peaks across the spectrum. These are detailed in Table 5.6. Closer inspection
Figure 5.40: Absorption spectra of phthalo blue from 1–20 THz. Inset: expanded view of 4.6 THz feature showing evidence of a double resonance.

of the absorptions reveals that, in fact, many are two sharp peaks overlaid. This is exemplified in the inset of Fig. 5.40. Changes in the crystal dynamics introduced in temperature dependence measurements further resolve these features and reveal even more oscillations completely overlaid at room temperature beyond the resolution limit of the experimental setup. These are detailed in later sections.

Phthalo green shows two significant sharp absorptions at 6.53 THz and 15.24 THz with a series of more subtle features from 7–15 THz as outlined in Table 5.7 and shown in Fig. 5.41. The spectrum of phthalo green also shows more information than is immediately obvious. The noise floor appears somewhat more significant than observed in phthalo blue, and other pigment samples measured in this setup. In fact, this ‘noise’ is actually weak oscillations being washed out by thermal populations. Low temperature measurements presented hereafter reveal these subtle vibrations.

Both pigments are comparatively highly transmissive across the entire spectrum. The spectral envelope increases with frequency typical of materials in this regime. Most pigment samples investigated reached cut-off below 15 THz. Phthalo blue and green have been somewhat anomalous in showing reasonable transmission out to
Figure 5.41: Absorption spectra of phthalo green from 1–20 THz.

Table 5.6: Phthalocyanine blue absorptions in the THz regime.

<table>
<thead>
<tr>
<th>Position (THz) (±.01)</th>
<th>Amplitude (±.01)</th>
<th>Area (±.05)</th>
<th>FWHM (THz) (±.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.72</td>
<td>0.22</td>
<td>1.08</td>
<td>0.14</td>
</tr>
<tr>
<td>3.93</td>
<td>0.06</td>
<td>0.67</td>
<td>0.31</td>
</tr>
<tr>
<td>4.55</td>
<td>0.34</td>
<td>3.06</td>
<td>0.25</td>
</tr>
<tr>
<td>4.66</td>
<td>0.32</td>
<td>2.36</td>
<td>0.30</td>
</tr>
<tr>
<td>7.01</td>
<td>0.14</td>
<td>0.88</td>
<td>0.18</td>
</tr>
<tr>
<td>8.56</td>
<td>0.47</td>
<td>3.29</td>
<td>0.20</td>
</tr>
<tr>
<td>9.15</td>
<td>0.10</td>
<td>1.27</td>
<td>0.35</td>
</tr>
<tr>
<td>10.57</td>
<td>0.59</td>
<td>3.61</td>
<td>0.17</td>
</tr>
<tr>
<td>13.02</td>
<td>0.49</td>
<td>2.64</td>
<td>0.15</td>
</tr>
<tr>
<td>15.17</td>
<td>0.69</td>
<td>4.04</td>
<td>0.16</td>
</tr>
<tr>
<td>17.15</td>
<td>0.45</td>
<td>2.40</td>
<td>0.15</td>
</tr>
<tr>
<td>19.12</td>
<td>0.38</td>
<td>3.62</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Both pigments are easily distinguishable at room temperature for frequencies in the 3–20 THz range. Thus THz techniques are a suitable tool for identifying between base $\beta$-CuPc and chlorinated variants. The stark contrast between spectra suggests that the full complement of CuPc pigments may exhibit a unique response to THz photons.

At this stage, it is unclear if the distinction in the THz spectra is resultant of the chlorination of the outer sites in the CuPc molecule, the forced crystal phase change.
in the halogenation process or a mixture of both. It is suggested that the higher intensity sharp vibrations of phthalo blue and green are consequence of motions centred on the outer hydrogen and chlorine atoms or librations of the planar porphine molecules. It is not expected these features are intermolecular oscillations as these would typically show broader spectral features.

Table 5.7: Phthalocyanine green absorptions in the THz regime.

<table>
<thead>
<tr>
<th>Position (THz) (±0.01)</th>
<th>Amplitude (±0.01)</th>
<th>Area (±0.05)</th>
<th>FWHM (THz) (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.17</td>
<td>0.09</td>
<td>0.53</td>
<td>0.17</td>
</tr>
<tr>
<td>6.53</td>
<td>0.29</td>
<td>4.24</td>
<td>0.41</td>
</tr>
<tr>
<td>4.55</td>
<td>0.34</td>
<td>3.06</td>
<td>0.25</td>
</tr>
<tr>
<td>9.98</td>
<td>0.07</td>
<td>0.54</td>
<td>0.21</td>
</tr>
<tr>
<td>11.21</td>
<td>0.08</td>
<td>0.38</td>
<td>0.14</td>
</tr>
<tr>
<td>15.24</td>
<td>0.87</td>
<td>4.60</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Temperature Dependence

Temperature dependence measurements taken at the Australian synchrotron for phthalocyanine pigments are illustrated in Figs. 5.42 and 5.48. For phthalo blue, minimal positional changes are observed with temperature. There is a slight hardening of features with low temperature, with the most pronounced shifts in the order
of 0.1 THz, seen in Figs. 5.43, 5.44, 5.45 and 5.46. Blue shifting of resonances is generally linear with thermal energy, barring the two features labelled peak 3 and peak 4. In these cases, a strong positional shift is found in the 200 K–300 K region while little to no movement is observed below 200 K. However, this must be interpreted with caution as these features are very closely spaced at high temperatures. In fact they only become truly resolved below 200 K. It is probable this phenomena is an artefact of peak fitting software struggling to truly differentiate the two structures at higher temperatures. A substantial dependence on temperature can be seen for the amplitude of most resonances. A $> 20\%$ increase is observed across the spectrum from 300 K down to 20 K, also shown in Figs. 5.43, 5.44, 5.45 and 5.46. Peaks 2 and 12 are the only features that do not increase in amplitude with decreasing temperature. Some variability is observed in the data but this is intrinsic to the experimental process and peak fitting software as opposed to corresponding to any real phenomena.

A drop in absorbance at 6.5 THz corresponds to a mis-match in removing spectral effects from the beeswax binder, which contains a temperature dependent absorption at this location.
Figure 5.43: Temperature dependence of position and amplitude for vibrational modes in phthalo blue pigment from 3-5 THz.
Figure 5.44: Temperature dependence of position and amplitude for vibrational modes in phthalo blue pigment from 5–9 THz.
Figure 5.45: Temperature dependence of position and amplitude for vibrational modes in phthalo blue pigment from 9–16 THz.
Figure 5.46: Temperature dependence of position and amplitude for vibrational modes in phthalo blue pigment from 16–20 THz.
Low temperature measurements also reveal a series of weaker sharp resonances, thinned out by thermal noise in higher temperature measurements. These arise at 5.1 THz, 7.6 THz, 12.5 THz and 12.8 THz, becoming apparent for temperatures below 200 K. Additionally, low temperature spectra confirm a series of closely spaced features speculated in room temperature measurements. The 4.55 THz and 4.66 THz resonances are confirmed as being two distinct peaks with the latter exhibiting a stronger positional temperature dependence, thus allowing clear resolution between the peaks for temperatures below 220 K. At 8.56 THz a realisation is made that this resonance contains a satellite in its right shoulder. This is hinted at 200 K and becomes obvious below 100 K. At 20 K a distinct resonance can be observed at 8.73 THz. Similarly, the 15.17 THz peak splits into two distinct resonances at low temperature. The distinction is not as obvious here, but two peaks can be resolved below 100 K. At 20 K the dual absorptions are located at 15.17 THz and 15.25 THz. Thus the latter feature exhibiting a blue shift with the former showing no temperature dependence permits the distinction at low temperature. These are illustrated in Fig. 5.47.

**Figure 5.47:** Peak splitting at low temperature in phthalocyanine blue pigment. At room temperature these correspond to: (a) 4.55 THz and 4.66 THz, (b) 8.56 THz and (c) 15.17 THz peaks at room temperature.

Temperature dependence measurements taken at the Australian synchrotron for phthalocyanine green pigments are shown in Fig. 5.48. Similarly to phthalo blue, phthalo green shows temperature dependence most prominent in the amplitude of
resonant modes. There is a hardening of the peak positions upon cooling, but this is less than 0.02 THz for both peaks.

Both the main resonances give a strong increase in amplitude with cooling. The 6.56 THz peak doubles in amplitude from 0.3 to 0.6, while the 15.2 THz peak increases by a third going from 0.9 to around 1.2. These increases are linear with temperature. For the 6.56 THz peak, the slight positional dependence on temperature is clear, however the exact relationship is somewhat clouded. A subsidiary peak in the right shoulder of this feature introduces asymmetry for temperatures above 150 K, reflected in a reduced accuracy in fitting this peak, which assumes gaussian symmetry about the central position.

Beyond the obvious resonances, a large number of unforeseen features emerge with low thermal energy. At room temperature these are obscured by thermal excitations appearing in what appears as a noisy baseline in the spectral profile. The most prominent of these vibrational modes appear at 7.73 THz, 8.56 THz and 12.06 THz. Additionally, in the 12–15 THz region numerous weak, sharp absorbances are present. These are emphasised in Fig. 5.50. These features appear progressively with cooling, becoming clearly resolved below 250 K.
Figure 5.49: Temperature dependence of position and amplitude for vibrational modes in phthalocyanine green pigment.

Figure 5.50: 11–14 THz range in phthalocyanine green pigments showing development of weak sharp resonances at low temperature. Each spectra is offset by 0.05 relative to its predecessor.
5.4.3 Conclusions

Terahertz spectroscopy has revealed a series of sharp resonant modes in blue and green phthalocyanine pigments. Temperature dependence of these features has been established, with modes generally strengthening and hardening at low temperature. Powder x-ray diffraction measurements have confirmed phthalocyanine blue pigment consisting the $\beta$ crystal polymorph, with phthalocyanine green composing the halogenated chlorine-copper phthalocyanine, isomorphic to the $\alpha$ phase.

Terahertz spectroscopy definitively distinguishes between these two variants, inviting further investigation to whether this differentiation is maintained across all crystal polymorphs and halogenated adaptations. Additionally, modelling and obtaining a physical origin of spectral absorptions is desirable, currently suggested as being dominated by sharp oscillations of the outer hydrogen and chlorine sites.

Experimental data also provides a strong distinction between phthalocyanine pigments and visibly similar pigments, such as ultramarine, cobalt and prussian blue. Thus, terahertz waves are a useful tool in identifying fraudulent pieces, where these pigments are concerned. They also provide a dating tool, with any artwork containing phthalocyanine post-dating 1935. Importantly, this can be achieved non-invasively and non-destructively without the complications involved in trying to obtain x-ray analysis.

Terahertz techniques are advantageous over visible and infrared modalities, also used in analysing these pigments. Visibly, with a wide array of binders, mixture concentrations and preparation techniques a single phthalocyanine pigment may cross many shades, making distinction with similar colours ambiguous. Terahertz photons can identify these. Furthermore, infrared techniques have inferior penetration depths, with terahertz spectroscopy allowing for a more holistic analysis.

Low temperature spectroscopy shows a slight hardening of vibrational modes in the order of 0.1–0.2 THz. A strengthening is of resonances is demonstrated with a reduction of thermal energy. Relative shifting between closely spaced vibrational modes with temperature allows resolution between these features, not feasible at
room temperature.

Terahertz spectroscopy gives valuable insight into phthalocyanine pigments, invites further research into a full understanding of phthalocyanines terahertz response while adding to the much needed database of information for terahertz usage in art conservation science.
CHAPTER 5. THZ SPECTROSCOPY OF ARTISTS' MATERIALS

5.5 Ochre Pigments

5.5.1 Introduction

Ochre pigments have been widely used across the globe and throughout the entirety of human history. Generally, they consist of various hydrated and dehydrated iron oxides together with other trace minerals.

The presenting iron oxides determine the overall pigment colour: red ochres primarily consist of the dehydrated Fe$_2$O$_3$ iron oxide, commonly known as hematite. Transitioning into yellow pigmentations corresponds to increases in the hydrated iron oxide Fe$_2$O$_3$·nH$_2$O, or limonite. A yellow-brown ochre pigment is resultant of the partially hydrated iron oxide FeO(OH) commonly named goethite. Finally, a high composition of the magnetic iron oxide Fe$_3$O$_4$, magnetite, will extend into a black pigmentation.

Characterising, identifying and analysing ochre pigments is pivotal in progressing art conservation science and understanding human history. The use of ochre stretches through history, with reports well documented of Neanderthals using manganese and iron oxides 40,000 – 60,000 yrs ago [164]. More recently, it is suggested the use of red ochre extends beyond to early Neanderthals 250,000 yrs ago, and could even provide clues in unlocking human evolutionary history [165]. The non-empheral nature of ancient ochre artefacts is important in understanding human ancestral behaviour. With such a long and rich history, ochres are found in archaeological sites all over the world. Critically analysing these materials have taken many forms: Laser Ablation Inductively Coupled Plasma Mass Spectrometry is employed in the Kenya Rift Valley assessing 43 ochre samples across 10 geographical locations [166]. X-ray fluorescence techniques reveal interesting insights into ochre paintings found at Pompeii. Heat from the eruption of Mt Vesuvius consequently forced a dehydration of yellow ochre to red ochre in sections of many artworks and paintings, with this research differentiating original red ochre paint to that dehydrated from the volcanic eruption [167]. Differentiation of artificial and natural red ochre (hematite)
has also been investigated in the Palaeolithic site, Riparo Dalmeri in north eastern Italy [168]. In Australia, x-ray fluorescence microscopy is used in characterising an array of ochre pigments used widely in aboriginal paints and indigenous artefacts [169]. Furthermore, raman spectroscopy, infrared spectroscopy in conjunction with electron and visible microscopy is utilised in critically analysing a series of so-called ‘x-ray’ aboriginal paintings, where the bones of the painted subject are emphasised, obtained from a rock shelter in Arnhem Land [170].

All of the aforementioned research areas, except in northern Italy (2011), have been performed within the last three years. Thus interest in these pigments is current and of huge consequence in understanding indigenous culture and more widely, the human story. THz understanding applied to these materials is still somewhat in its infancy, but stands to complement and give added insight as THz techniques develop and strengthen. The safe, non-invasive and non-destructive analysis offered by THz photons is not replicated in x-ray techniques, which also generally require the support of large research facilities, like synchrotrons. Additionally, THz waves penetrate deeper into items of study compared to infrared and visible light while giving the added benefit of simultaneous time domain imaging of multiple subsurface layers.

5.5.2 Composition Analysis

Understanding the precise composition and classification of ochre pigments is highly contentious. The lack of uniformity and a clear naming system is severe. This is consequence of several factors. Firstly, independent of the colour index, these pigments are usually named in some combination of their visible colour (red, brown, yellow etc), a characteristic property, (transparent, bright etc), production method (raw, burnt etc) and/or geographic location (Australia, Italy etc). This method generates similar, if not the same, descriptors for many pigments even though they may belong to a different colour index. Secondly, there is an added layer of complexity in that many of the outlined descriptors consist of many contemporary and traditional
names, interchanged seemingly at random. Further convolution is observed when factoring that these are applied across many different spoken languages. These together generate multiple names for the same pigment as well identical names for many pigments.

Let us look at PR101 and PR102 as examples. On the pigments database [171] a non-exhaustive list gives 171 and 130 different names for PR101 and PR102 respectively. On the other hand, investigating the name 'Raw Sienna' reveals exact matches in the colour index for PR102, PY42, PY43, PBr6 and PBr7. Thus a single name is used not only across five colour index identifiers but also across three different colours (red, yellow and brown). This is only a small taste of the overall difficulty of understanding the nomenclature and exact composition of each ochre pigment. This is summarised by the pigment database who quote that the ochre names/composition have become “an almost impossible list of varied phrases” [171].

With this in mind, caution must be taken in interpreting the direct composition of the pigments obtained. All ochre pigments were purchased from Langridge. The information given by this supplier will be used as a starting point, in conjunction with information presented on the pigments database. A summary of each investigated ochre is presented in Table 5.8.

Australian and red ochre are both natural inorganic pigments. Their red colour is resultant to a large proportion of the red iron oxide, Haematite (Fe₂O₃) [147, 171], present in the pigment. Both pigments are listed as consisting over 90% haematite, along with other minerals. These minerals are dependent on the clay/earth used in making the pigment and also the geographical region. Australian ochre, as the name suggests, is derived from Australian soil, whereas red ochre is derived from Indian soil. Other minerals that may be present in this pigment include quartz, calcium carbonate, goethite and gibbsite.

The yellow series of pigments: transparent yellow oxide, yellow ochre, golden ochre and orange ochre are all given to consist of the same material by the supplier. This is consistent with the pigments database which suggests that PY42 and PY43
Table 5.8: Ochre pigments investigated in the THz regime.

<table>
<thead>
<tr>
<th>Proprietary Name</th>
<th>C. I. Name</th>
<th>Composition</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Ochre</td>
<td>PR101</td>
<td>native iron oxide (Ind.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Australian Ochre</td>
<td>PR102</td>
<td>native earth (Aus.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Trans. Yellow Oxide</td>
<td>PY42</td>
<td>prepared iron oxide</td>
<td>synthetic inorganic</td>
</tr>
<tr>
<td>Yellow Ochre</td>
<td>PY42</td>
<td>native earth (It.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Golden Ochre</td>
<td>PY43</td>
<td>native earth (It.)</td>
<td>synthetic inorganic</td>
</tr>
<tr>
<td>Orange Ochre</td>
<td>PY43</td>
<td>native earth (It.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Mars Brown</td>
<td>PBr6</td>
<td>prepared iron oxide</td>
<td>synthetic inorganic</td>
</tr>
<tr>
<td>Raw Umber</td>
<td>PBr7</td>
<td>native earth (Cyprus)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Raw Umber Light</td>
<td>PBr7</td>
<td>native earth (It.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Burnt Umber</td>
<td>PBr7</td>
<td>native earth (Cyprus)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>PBr7</td>
<td>native earth (It.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Cassel Earth</td>
<td>PBr7</td>
<td>native earth (It.)</td>
<td>natural inorganic</td>
</tr>
<tr>
<td>Roman Black</td>
<td>PBk11</td>
<td>native earth</td>
<td>natural inorganic</td>
</tr>
</tbody>
</table>

are essentially a single pigment, with huge overlap in composition. Their yellow
colour is consequence of their limonite composition. Limonite consists of a series
of hydrated iron oxides, with a chemical formula of FeO(OH)·nH₂O. All pigments
are given as being close to 100% limonite. Yellow, golden and orange ochre are all
derived from Italian soils, with golden ochre being a synthetically derived variant.
Transparent yellow oxide is an independently prepared synthetic pigment.

The brown pigments are somewhat sporadic. Raw umber, raw umber light,
burnt umber and raw sienna are all attributed to having similar contents. These are
hematite (50–70%), manganese dioxide (0–15%), limestone (0–10%), carbon (0–5%)
and quartz (0–5%). Cassel earth is considerably unclear in its composition, given
only as 100% iron oxides and clay silicates. Mars brown is said to be a mixture of
iron oxides in the following proportions: 30–50% of Fe₂O₃·nH₂O (PY42), 10–20% of
Fe₃O₄ (PBk11) and 20–40% of Fe₂O₃ (PR101).

For the only black pigment investigated, roman black, no clear composition is
given. It appears as though it predominately consists of Fe$_3$O$_4$, commonly known as magnetite, along with carbonates of calcium, manganese and iron.

Looking at this scenario from a different perspective, it appears a better understanding of the composition can be achieved when considering the overall colour of the pigments holistically. In general redder ochre pigments gain their colour from the red dehydrated iron oxide Fe$_2$O$_3$ (hematite), solid bright/strong yellow pigments gain their colour from the hydrated iron oxide FeO(OH)$\cdot$nH$_2$O (limonite). A transition into dull yellow, earth toned and brown pigments is seen with an increase in the partially hydrated iron oxide FeO(OH) (goethite). Finally, the colour palate is extended into black pigmentation with a strong Fe$_3$O$_4$ (magnetite) content. More subtle variations in the pigmentation are observed with added manganese (sienna and umber) and by heating to transfer the hydrated iron oxides into the more red hematite (burnt variants). A third layer of subtle tonal shifts are found due to trace minerals and compounds consequence of the regional uniqueness of each mined pigment.

For analysing the THz characteristics, the descriptors for each pigment will be kept to the proprietary name as going beyond this level invites misinterpretation and the possibility of misleading results. As will be seen in the THz spectra below, the C. I. names are prone to discrepancy and incorrect identification.

5.5.3 Results

Terahertz Spectroscopy

Absorption spectra for Australian and red ochre pigments are shown in Fig. 5.51. Spectra are similar across the range. Four large characteristic absorptions are observed at 9.8 THz, 11.8 THz, 13.9 THz and 16.2 THz. At 7.0 THz a small, much sharper absorption is also present for both pigments.

Despite the overall similarities, subtle variations can be seen. Red ochre hints towards a second spectral feature in the region of 6.5 THz. Furthermore, in both the 9.8 THz and 11.8 THz peaks Australian ochre appears to have a broader shoulder on
the lower frequency side. This may be extra weak absorptions in this pigment. Temperature dependence measurements presented later aim to reveal further information on these claims. The overall absorption envelope is somewhat differing between the pigments. Red ochre is more absorbing in the low frequency region <7 THz, however Australian ochre is significantly more absorbing for frequencies above this. It is difficult to attribute the overall profile as characteristic of the pigment, as the particulates in the sample are of the order of the wavelength. Thus, it is likely the increased absorption is consequence of scattering.

The THz database [172] and [10] present THz data for hematite for the region below 12 THz. The spectral data does not immediately match that observed in Fig. 5.51. The 7 THz feature is hinted in both cases but is not definitive. Further, the 9.8 THz feature is not apparent. Despite the apparent discrepancy, it is still believed that the features observed for these pigments is due to the hematite content, which should be close to 100%. Both complementary sets of data have comparatively high transmission, thus a lower concentration of hematite. This explains the apparent ‘washing out’ of the 7 THz peak. As well as that, the 9.8 THz feature appears at the limit of their presented data. This, coupled with a much lower concentration, could explain why these absorptions are not replicated in these works.

Figure 5.51: THz spectroscopy of Australian ochre and red ochre pigments with synchrotron radiation.
In Figs. 5.52 and 5.53 synchrotron data is shown for the pigment yellow class (PY42 and PY43) of iron oxide ochres, namely yellow ochre, orange ochre, golden ochre and transparent yellow oxide. Interestingly, the supplier claim that all these pigments are closely consistent in their composition is not supported by the THz spectra. Golden, orange and yellow ochre are largely similar as expected, however transparent yellow oxide is profoundly different.

Considering Fig. 5.52, the three pigments share strong vibrational resonances
at 3.6 THz, 8.2 THz, 9.2 THz, 12.1 THz, 13.9 THz and 18.1 THz. They also share a complex of closely spaced sharp peaks in the 5–8 THz region. Golden ochre is a synthetically derived pigment sharing a closest resemblance to yellow ochre, its naturally mined counterpart. Thus it appears THz photons are unable to consistently distinguish between natural and synthetic pigments of this type. However, orange ochre (natural) shows an extra absorbance at 16.3 THz, a stronger peak at 13.9 THz and also does not observe the ‘roll off’ in absorbance from 12.2–13.5 THz. These are attributed to trace minerals and compounds specific to this pigment, likely dependent on the geographical location of the earth mined for this pigment. Thus, THz can distinguish minor changes in the mineral composition of yellow ochre pigments.

An interesting result is emphasised in Fig. 5.53, where transparent yellow oxide, given to have an identical composition as the other three yellow pigments, shows a completely unique THz spectrum. The only consistent feature between this pigment and its counterparts is the 8.2 THz absorption. However, even this is not entirely consistent. In transparent yellow oxide the peak is much broader, with a 0.87 THz FWHM as opposed to 0.46 THz in the other pigments. With the intrinsic poor nomenclature in identifying these pigments attributing this discrepancy to a real phenomena is difficult. There are two likely reasons: firstly, the pigment is simply labelled incorrectly based off its visible characteristics as opposed to its true chemical composition. Secondly, it is possible that being an entirely prepared synthetic pigment results in many natural minerals and composites being excluded from the final product. If these have strong features in the THz region then this would significantly alter the spectrum. However, given no strong similarities appear between the spectra this option seems less likely. Visually, transparent yellow oxide is much darker in colour, closer to brown/earth tones, thus is further not likely to consist of limonite, as suggested. Without a THz database for these materials or extensive research into the physical origin of features the solution to this discrepancy remains clouded.

THz spectra for the brown and black pigment classes are shown across Figs. 5.54,
5.55, 5.56 and 5.57. These pigments are generally distinct despite their similar colour index. Counter intuitively, the only spectra with similar features across the range are from separate colour indices, namely cassel earth (PBr6) and roman black (PBk11) in Fig. 5.57.

Looking at Fig. 5.54 the compositional claims made by the supplier are not reflected in the THz spectra. Raw sienna, raw umber and raw umber light are all allegedly consisting of above 50% hematite ($\text{Fe}_2\text{O}_3$). However, no suggestion of the hematite features observed in Fig. 5.51 are replicated in these pigments. Thus it is likely the hematite content is somewhat lower than quoted. Furthermore, each individual pigment is unique. Raw sienna exhibits a broad absorption centred on 8.3 THz with a complementary set of weaker resonances at 3.6 THz, 4.9 THz, 6.3 THz and 7.1 THz. Interestingly, these weaker features coincide with a similar region to those observed in yellow, orange and golden ochres. Temperature dependence measurements will investigate this further to establish if this correlation has a consistent underlying cause. Raw umber light consists a solitary broad absorption at 8.2 THz, whereas raw umber shows a weaker peak at 6.4 THz and a large, broad feature centred at 8.5 THz, which appears to be two barely resolved absorption peaks. Raw
umber (Cyprus) and raw umber light (Italy) are derived from significantly different geographical locations, which could further explain their spectral dissimilarities.

![Figure 5.55: Comparison of Australian ochre, burnt umber and raw umber pigments.](image)

The spectral characteristics for burnt umber (Fig. 5.55) are consistent with expectation. The ‘burnt’ varieties refer to pigments which, upon heating, see much of their hydrated iron oxides transform to the dehydrated hematite, giving them a redder tone. Experimental data reflects this with the burnt umber spectrum seen as a transition between raw umber and Australian ochre. The 9.8 THz and 13.9 THz features are developing, while hints of the 7 THz and 11.8 THz are observed. Temperature dependence measurements are expected to verify the subtle modes.

Mars Brown pigment presents an interesting case (Fig. 5.56). A single sharp absorption is present at 8.7 THz. This is unique compared to all other presented pigments. Like transparent yellow oxide, mars brown is a fully synthetic prepared pigment. Thus it appears these types of pigments vary drastically in their spectral properties when compared to naturally mined pigments.

As illustrated in Fig. 5.57, roman black and cassel earth display similar spectra despite being found in different colour indices. Strong vibrational modes are seen at 3.2 THz, 6.9 THz, 9.5 THz and 14.0 THz. Roman black gives one more resolved
feature at 15.8 THz not seen in cassel earth. The features are more pronounced in roman black, despite both pigments having a similar absorption envelope. Both pigments are quite dark in colour, thus the features are attributed with a strong Fe₃O₄ content. Although, neither pigment is definitive in containing high concentrations of this oxide, Fe₃O₄ is ferrimagnetic and a simple laboratory test showed both pigments are strongly attracted to a permanent magnet, supporting the claim. Roman black
is a stronger black pigment than cassel earth, reflected in their classification. This also supports the hypothesis that these features are resultant of the magnetite iron oxide, with roman black showing comparable more distinct and stronger absorption features.

Overall, room temperature THz spectra show clear distinction across a range of iron oxide ochre pigments. Vibrational modes are found across the spectrum. THz photons are sensitive to the composition of the pigment and provide useful insights into the constituents of each material beyond what is immediately given by the supplier. Further, subtle variations in similar pigments, suggest THz techniques may be adequate in identifying the geographical source and processing procedures of materials.

**Temperature Dependence**

This section presents temperature data obtained at the Australian Synchrotron. All spectra show varying degrees of temperature dependent features and provide much needed insight beyond what is immediately obvious in room temperature experimental data presented previously, and in literature.

![Figure 5.58: THz spectroscopy of Australian ochre pigment from 20K–300K with synchrotron radiation.](image)

Australian ochre shows reasonable temperature dependence across the spectrum.
In Fig. 5.58, lower intensity absorptions at 7.0 THz and 11.8 THz show a slight blue shift of 0.1 THz in cooling from 300 K to 20 K. The 11.8 THz peak appears to subtly sharpen with cooling, with a consistent intensity. Conversely, the 7.8 THz peak sharpens and increases in amplitude by around 25% upon cooling. It is difficult to accurately analyse the temperature characteristics of the more prominent absorptions as the transmitted signal in these cases approaches the noise floor of the experimental setup. The shoulders of each peak show subtle shifts consistent with the peaks moving to higher energies. Evidence of sharpening of the spectral features is also present.

![THz spectroscopy of red ochre pigment from 20 K–300 K with synchrotron radiation.](image)

Red ochre shows a similar temperature dependence to its Australian counterpart, displayed in Fig. 5.59. The 7 THz absorption also blue shifts by 0.1 THz and sharpens, with a increased intensity in the vicinity of 25% with cooling to 20 K. The 11.8 THz absorbance exhibits double the shift to 12.0 THz, not in agreement with Australian ochre. However, hesitation is placed on this claim, as asymmetry in the feature gives a skewed appearance towards higher photon energy. Careful inspection of this phenomena, shows evidence of multiple closely spaced sharp features in this region developing with low temperature, beyond the resolution limit of the experimental setup. This is not evidenced in Australian ochre, thus reservation is taken
in drawing direct comparison between these pigments centred on this feature. As with Australian ochre, the large peaks reach the absorption limit if the system, but the shoulders also hint towards a higher energy shift at lower temperatures.

![Figure 5.60: Comparison of 6.8 THz region of Australian ochre and red ochre. (a) Australian ochre does not show secondary feature, (b) red ochre showing existence of secondary feature.](image)

The THz distinction between the two visually similar pigments hypothesised with room temperature measurements is confirmed in low temperature spectra. Fig. 5.60, emphasises this distinction in the 6–7.6 THz region. The broad shoulder observed at room temperature in red ochre is revealed to be a vibrational mode unique to this pigment. This mode strengthens and sharpens with low temperature. Consistent with other observed features, this peak shifts to higher frequency as thermal energy is reduced. At 300 K the vibration is centred in the region of 6.4 THz and approaches 6.6 THz at 20 K. Overall, temperature dependence confirms that THz spectroscopy is sufficient in identifying between geographically separate hematite based ochre pigments, despite their visual similarities.

Temperature dependence of the native earth yellow pigments is shown in Figs. 5.61, 5.62 and 5.63. As with the room temperature spectra, yellow ochre and golden ochre show identical spectra at 20 K. Furthermore, their full temperature characteristics are consistent. Thus THz photons cannot distinguish these pigments, but still show immense features, temperature dependence and insight into the structural properties of the pigment constituents. Orange ochre further exhibits subtle differentiation as was present in room temperature measurements.
Figure 5.61: THz spectroscopy of yellow ochre pigment from 20 K–300 K with synchrotron radiation.

In the 0–10 THz region the pigments remain indistinguishable. The 3.60 THz resonance softens in all pigments to 3.47 THz. In the 5–8 THz resonances strengthen considerably with a simultaneous blue shift. Thus, these peak, which were unclear at room temperature can now be easily resolved. Above 10 THz a new pronounced absorbance rises at 11 THz with decreasing temperature. Distinction is observed with the development of this resonance in the orange ochre pigment. Less clarity is present in this feature, appearing to be distorted by nearby satellites. In room temperature spectroscopy, a 16.3 THz extra vibrational mode is present in orange ochre. Low temperature spectroscopy reveals that this feature is not unique to this pigment, but is much weaker in its natural pigment counterparts. The same can be said for the 17.4 THz mode. Nonetheless, these spectra still support the case for differing compositions despite supplier and colour index classifications. Furthermore, low temperature spectra results in extra low amplitude resonances located at 10.2 THz, 10.5 THz and 13 THz. Thus, overall the three pigments are closely related in their composition, especially yellow and golden ochre, essentially indistinguishable across the spectrum even with temperature measurements. Orange ochre displays subtle differences in spectra, exaggerated in low temperature measurements indicating a compositional variance in dispute of external classifications.
In transparent yellow oxide (Fig. 5.64), absorption features show consistent shifts to higher photon energy across the spectrum. Furthermore, a new vibration mode is discovered at 17.2 THz. This first becomes apparent at 200 K, illustrated in Fig. 5.65. The absorption strengthens with further cooling, but shows no positional variation.

The 8.2 THz absorption peak in transparent yellow oxide shows a linear blue shift from 8.22 THz to 8.39 THz over 300 K–20 K range. The peak amplitude also
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Figure 5.64: THz spectroscopy of transparent yellow oxide pigment from 20 K–300 K with synchrotron radiation.

Figure 5.65: New absorption peak discovered in transparent yellow oxide with low temperature.

exhibits a linear increase shown in detail in Fig. 5.66. At 11.2 THz the absorption shows a slight shift to higher frequency of around 0.1 THz. Features centred at 12.5 THz and 14 THz show strong movements to higher photon energies however, being at the detection limit of the system, were not able to be fitted accurately. The feature centred at approximately 14 THz shows a blue shift in the vicinity of 1.5 THz. Interestingly, none of the features seen in the other ‘pigment yellow’ colorants become visible in low temperature measurements of transparent yellow
Figure 5.66: Temperature characteristics of the low frequency resonance in transparent yellow oxide showing location and amplitude.

oxide. This strengthens the claim of a strong compositional dissimilarity in the prepared synthetic pigment when compared to its native earth counterpart.

Figure 5.67: THz spectroscopy of mars brown pigment from 20 K–300 K with synchrotron radiation.

In Fig. 5.67, temperature measurements for mars brown pigment reveal a large amount of previously unforeseen information. In room temperature measurements a series of ‘wobbles’ in the low frequency profile are observed but indistinguishable from noise. These are revealed to be a series of low intensity absorptions that become resolved with the removal of thermal noise. Furthermore another resonance becomes apparent located on the left shoulder of the large sharp 8.7 THz resonance. All these
features are observed to harden with low temperature, between 0.1–0.2 THz, shown in Fig. 5.68. These shifts are observed to be linear with temperature. The absorbances also increase in intensity as lower temperatures are present. Also, in the 15 THz region a brief increase in transmission is apparent. However, with nearby regions highly absorbing drawing any significant conclusions pertaining to this observation become impossible.
Figure 5.68: Temperature dependence of position and amplitude in mars brown pigment from 6–7 THz.
Figure 5.69: Temperature dependence of position and amplitude in mars brown pigment from 7–9 THz.
Fig. 5.70 shows the full temperature spectrum for raw umber pigment. Previously reported spectral absorbances are observed to blue shift with low temperature. These are detailed in Fig. 5.71. The 6.4 THz feature shows a strong sharpening in the presence of low temperatures. Similar responses for the 8.3 THz and 8.8 THz modes results in these features not becoming better resolved as expected with the reduction of thermal noise.

Detailed data for the temperature response of raw umber pigments is shown in Fig. 5.71. All location and absorbance movements appear overall linear across the spectrum. Inherent noise is observed in the 8 THz data due to the difficulty in separating these absorptions with peak fitting software. The low frequency resonance shows the strongest shift but only a small increase in amplitude. Both the 8 THz features show a blue shift of around 0.15 THz, with the higher frequency mode giving a 50% relative stronger increase in absorbance, allowing for a degree of differentiation between these resonances.

In raw umber light, minimal temperature dependence is observed. However, the singular broad absorption at 8.1 THz shows a linear hardening with decreasing thermal energy. There is no dependence observed in any other peak characteristics however. Beyond this there is no change in the overall spectral profile nor do any
Figure 5.71: Temperature dependence of position and amplitude of raw umber pigment.
extra resonances appear with cooling. This confirms the significant compositional differences between this pigment with the standard raw umber and further contradicts the supplier claim that these are made of identical constituents. No consistency between observed vibrational modes or temperature response is observed.

The temperature response of burnt umber, given in Fig. 5.74, supports the claim of this pigment containing hematite resultant of its production process. The large absorbing region centred at 10 THz shows minimal changes with temperature. Interestingly, the low frequency absorption at 7.1 THz, the same as in Australian and red ochre, hypothesised in room temperature spectroscopy is confirmed in lower
temperature measurements. Thus, consequently a large degree of certainty is now present in attributing these features to hematite iron oxide. Outside of this, no further temperature characteristics or useful new information is obtained.

In raw sienna (Fig. 5.75), a very strong temperature dependence is present, particularly in the region below 10 THz. Absorptions are seen to sharpen considerably, with some exhibiting red shift, others blue shift while one resonance does not shift. Furthermore, unforeseen features at room temperature become apparent upon cool-
ing. With weak features that wash out considerably towards room temperature peak fitting is not accurate here, thus analysis will keep to the raw data. The 3.60 THz resonance strongly red shifts to 3.45 THz, while sharpening and increasing in amplitude by around 15% at 20 K. At 4.9 THz, this peak is observed to be stationary with temperature, showing a slight increase in intensity. The 6.3 THz feature shows dramatic changes with cooling. A strong blue shift to 6.6 THz in conjunction to considerable changes in the overall peak profile with low temperature are apparent. The 7.1 THz resonance also shows similar characteristics in its hardening to 7.25 THz. The large absorption centred at 8.3 THz also evidences a hardening upon cooling, but as this absorption is too high, reaching detection limit, precise detail here is omitted.

![Graph](image.png)

**Figure 5.76:** New absorption peaks discovered in raw sienna with low temperature. Each spectrum is offset by 0.1 relative to its predecessor.

Two new spectral features were revealed in cooling the sample. These are shown in Fig. 5.76. These are observed at 5.3 THz and 5.8 THz. The 5.3 THz peak becomes apparent below 240 K, while the 5.3 THz is only visible for temperatures below 100 K. Both features hint at a slight blue shift as the temperature is further reduced beyond the point at which they become resolved.

Temperature dependence of cassel earth and roman black pigments is shown
in Figs. 5.77 and 5.78. The similarities in spectral features are further reflected in the temperature measurements. Furthermore, subsidiary subtle differences between the pigments become evident at low temperature. The mixture of cassel earth’s magnetite content with other iron oxides gives rise to subsequent minor features in the low temperature profiles. A weak absorption at 5.85 THz and slightly stronger resonance at 6.60 THz become more pronounced in the cassel earth as does a broad feature centred on 8.33 THz. These are still hinted in the spectra for roman black.

In these spectra there appears to be two competing profiles, one for the Fe$_3$O$_4$ and one for the deeper brown, goethite iron oxides. In the roman black, the Fe$_3$O$_4$ features dominate, whereas in cassel brown, the latter features come into prominence. This is exemplified in the temperature measurements.
Figure 5.78: THz spectroscopy of roman black pigment from 20 K–300 K with synchrotron radiation.

Figure 5.79: Temperature response comparison of 3.3 THz and 7 THz absorptions from 20 K–300 K for roman black and cassel earth pigments.
Peak fitting of the most prominent resonances across both pigments at 3.3 THz and 7 THz is shown in Fig. 5.79. Here it is seen that both features behave similarly in their positional and amplitude dependence on temperature, with cassel earth giving an overall lower peak amplitude, reflective of its lower Fe$_3$O$_4$ composition. Peak positions exhibit a linear dependence, with a much stronger hardening observed in the 7 THz resonance. The 3.3 THz peak shows a very weak blue shift with a lowering of temperature.

Overall a consistent blue shift is seen across the spectrum in both pigments. The only exception is the 5.8 THz low temperature feature in cassel earth. Despite the need for a reduction in thermal noise to completely resolve this feature, there is no subsequent link between the characteristics of this resonance with temperature.

### 5.5.4 Conclusions

The feasibility of terahertz spectroscopy in analysing iron oxide ochre pigments has been demonstrated. Many of the iron oxides and mineral materials used in these pigments have ‘fingerprint’ spectral features allowing pigment identification beyond what it immediately presented by the supplier. The four main iron oxide constituents of these pigments, hematite, limonite, goethite and magnetite show unique spectral profiles. Strong differentiation is demonstrated between prepared synthetic and natural forms in identical pigment classes. Furthermore, subtle variations of similar pigments with geographical separation is revealed. Finally, processes converting the iron oxides between hydrous and anhydrous forms can be tracked with THz photons. This invites further research into developing a categorical database of these materials in the THz regime, in conjunction to encouraging terahertz spectroscopic investigation of indigenous artefacts and cultural heritage items, based on these earth pigments. Terahertz techniques show advantages over competing modalities with higher depth penetration than infrared, and ease of use over x-rays.

Temperature spectroscopy has substantiated and confirmed the subtle variations and claims made in room temperature measurements. Distinction is confirmed be-
tween red ochre and Australian ochre as well as orange ochre with yellow and golden ochre. As well as that, various new vibrational modes are revealed at low temperature. Spectral features exhibit a general shift to higher photon energies with lower thermal energy. This gives stronger insight into the fundamental physical origin of spectral features.
Chapter 6

Conclusions

Terahertz spectroscopy has been shown to be highly useful when applied to 3D printing and art conservation science.

In 3D printing materials, high impact polystyrene is the most useful commercial printer filament. It consists of a low absorption coefficient giving a useable range up to 1.3 THz, while remaining relatively easy to print and mechanically robust. Polypropylene and polycarbonate also showed a high useable bandwidth, however unfavourable thermal properties and large print difficulties detract from their feasibility. Interestingly, nylon, PLA and polycarbonate modified filament gave similar transmissive properties, with the subtle variations reflected in their refractive indices. This indicates the improvement in mechanical and printing quality does not sacrifice the optical viability for terahertz photons.

The utility of 3D printed diffractive optics for terahertz systems was verified. Diffraction gratings made in PLA gave strong terahertz transmission, remained mechanically robust and gave outputs at ±30 degrees correlating strongly with theory. Tested lenses showed too high transmissive losses to be useful, however, improvements could be made in printing them in a lower-loss material.

Using inkjet 3D printing technology with superior resolution showed the possibility of extending into much more complex dielectric structures with finer detail. A hyperuniform waveguide was printed with 200 μm walls and verified to exhibit sufficient photonic band gap guidance. A careful model development and processing
procedure was needed to ensure success of this device. The geometry of the waveguide was at the limits of this process, thus walls were thicker than the attempted 100 µm resolution. The multijet variant of using photopolymerisation was shown to out perform standard stereolithography methods.

The terahertz response of synthetic and natural pigments showed very encouraging results. Polymorphs of quinacridone, verified by powder x-ray diffraction, were shown to have ‘fingerprint spectra’ useful in identification, fraud detection and dating. A sequence of resonances are revealed in the 1–12 THz region corresponding to wagging, twisting and rocking of the quinacridone benzene rings. A strong in plane rocking motion is found in each pigment between 7–9 THz. Strong agreement is found between experimental data and solid state density functional theory modelling. Spectral features of γ-QA and 2,9-DMQA are offset reflective of their isomorphism. Features show temperature dependence, generally a blue shift of 0.1–0.3 THz with cooling. However, some exceptions show a slight red shift.

Phthalocyanine pigments give a series of sharp resonances across terahertz frequencies. Distinction is found between β copper phthalocyanine and chlorinated copper phthalocyanine, isomorphic to the α crystal polymorph. These are also verified from powder x-ray diffraction. This suggests identification of the various crystal polymorphs and halogenated modifications is achievable. Temperature dependence reveals splitting of closely spaced resonances with corresponding weak blue shifts. Reduction of thermal noise shows the emergence of a series of weak sharp peaks in chlorinated copper phthalocyanine.

In ochre pigments, terahertz spectroscopy from 1–20 THz has demonstrated a more robust identification method than proprietary labelling and classifications. Strong distinction between natural ochres and synthetic variations is demonstrated. The four main iron oxide components: hematite, limonite, goethite and magnetite based pigments have all shown identifiable characteristics. Further subtle variation is observed from geographically isolated pigments of similar content. Thus, terahertz photons can distinguish these pigments as well as identify their geographical origin.
Temperature measurements consolidate assertions of subtle features at room temperature and show large dependence across the spectrum for many of these pigments, especially the limonite based ochres.

Overall, results stemming from terahertz photons have given invaluable insight into the fields of 3D printing and art conservation science, unavailable from competing spectroscopic modalities. This will only strengthen as terahertz methods improve alongside advancements in 3D printing methods and the continual improvements in understanding of the physical origins of terahertz spectral features in materials pertinent in art conservation science.
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