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Application of Broadband, Time-Resolved Magneto-Optics to Problems in Ultrafast Photophysics

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Abstract

Ever faster computers require ever more efficient data storage technologies. A major bottleneck for faster data storage in magnetic media is the speed at which magnetisation can be manipulated. To circumvent this, a better understanding of magnetisation and magnetic materials on ultrashort timescales ($10^{-15}$ – $10^{-9}$ s) is required. Pump-probe spectroscopy allows us to measure the response of systems to an optical stimulus over such times. When combined with magneto-optics, this provides a valuable method for investigating ultrafast magnetisation dynamics. A promising group of materials for future technologies is that of 2D materials, where the reduced dimensionality can cause them to have different properties to their 3D counterparts. Cr$_2$Ge$_2$Te$_6$ (CGT) is a recently discovered 2D ferromagnetic semiconductor which is a potential system for studying and understanding magnetism on ultrashort timescales. Transient ellipticity and transmittance spectra of a small, thin, single crystal of CGT were measured at 20 K, well below the Curie temperature of $\sim$63 K. Strong wavelength dependence was observed in the transient ellipticity spectrum, meaning that the ellipticity change was proportional to not only magnetisation change. The spectrum could be decomposed into the contributions arising from photoexcited electrons and demagnetisation, both of which showed very different dynamics.

Magnetic fields in a medium influence the polarisation of transmitted light through magneto-optic phenomena. Most studies of ultrafast magnetism use only single wavelengths to probe samples, which can miss the vital information that broadband spectra can provide. I have therefore built a broadband, ultrafast spectrometer that can measure transient polarisation change with a 350–750 nm, 200 fs supercontinuum probe. Ellipticity change is measured through the change in transmittance of a circularly po-
larised probe pulse when an applied magnetic field is reversed. Similarly, the transient ellipticity change is found from the change in transient transmittance. Rotation can be measured in a similar manner. To compare performance relative to other published instruments and validate its correct operation, the spectrometer was tested on various samples, from ferromagnetic films to paramagnetic ions in solution.

Porphyrrins are organic, naturally occurring compounds which show rich ellipticity and absorbance spectra so their photophysics are well studied. Zinc tetraphenylporphyrin, a member of this family of compounds, shows a strong ellipticity spectrum at room temperature and undergoes intersystem crossing from singlet to triplet states upon photoexcitation. Ultrafast electronic changes may therefore result in transient changes to the ellipticity, which could be measured with the above setup and compared to the transient absorbance. Broadband ellipticity spectra of the complex in solution were measured and the transient depopulation of the ground state was observed through a signal with the same shape as the ground state ellipticity spectrum. Furthermore, transient ellipticity spectra whose dynamics corresponded to an excited singlet state could be observed.
Magnetism lies at the core of many modern technologies. One such use of magnetism is data storage, which typically uses thin films made of many tiny magnets. Data is stored through the orientation of the magnets, through a system known as binary - magnets pointing up may represent 0, and down 1. Reversing one of these magnets is how new data is written. The speed of modern computers is limited by the rate at which they can read and write data; the rate at which the orientation of the magnets can be reversed. To improve this efficiency, we first need to be able to measure how magnetism behaves on so called ”ultrafast” timescales ($10^{-15} - 10^{-9}$ s), which can only be done using polarisation of light. For comparison, light takes roughly $10^{-13}$ s to cross a human hair. A polarised ray of light has an electric field which oscillates in a particular direction. When this light interacts with a material in a magnetic field, the direction of the oscillation changes. Therefore, by measuring the change in polarisation, the magnetic field of the sample can be measured.

The frequency at which the electric field oscillates defines the colour and energy of the light. Electrons occupy discrete energy states around atoms and can move between states by absorbing light of a particular frequency. Materials of different colours absorb different frequencies of light, so the amount of light absorbed at each frequency can tell you about the properties of the material. For example, chlorophyll in plants absorbs blue and red light, and so appears green. In a similar manner, the magnetic field affects the polarisation of different colours of light differently. This polarisation information can give us more insight into a materials’ electronic and magnetic structure.

For measurements on these ultrafast timescales, pump-probe spectroscopy is needed. Here, two pulses of light from a laser are used, a strong ”pump” pulse and a weaker...
"probe" pulse. First, the pump pulse passes through the sample, exciting it. Then, the probe pulse passes through the sample, measuring the absorption or polarisation change. By moving a mirror, the time-delay between the two pulses can be finely controlled, allowing us to observe how the polarisation and absorption spectra change after the pump pulse hits the sample. The second chapter of this thesis describes the development, implementation and testing of such a pump-probe spectrometer. The novel aspect of this spectrometer is that the probe pulse comprises a wide range of frequencies, all of which are measured at once. This means that we can quickly and precisely measure absorption and polarisation change as a function of both time and frequency.

A promising new group of materials for magnetic applications are layered magnets. On a structural level, these materials are formed of atomically thin layers, stacked on top of one another; this gives them interesting properties as the layers can only weakly interact with each other. One of the first such materials to be discovered was $\text{Cr}_2\text{Ge}_2\text{Te}_6$, which is magnetic as a single layer. In the third chapter of this thesis, a small crystal of this material is excited with a pump pulse, after which I measure how its magnetism gets weaker over time. As the pump-probe setup described above can measure a range of frequencies, the electronic structure of the excited state, and its magnetism, can be measured simultaneously.

Polarisation spectroscopy can also be used to investigate non-magnetic materials. As polarisation change and absorption spectra are sensitive to different material properties, measuring both allows for the electronic structure of a material to be measured more accurately. Porphyrins are a large group of molecules that are responsible for both the red colour of blood and the green of chlorophyll due to their strong interaction with light. Due to this they have been studied extensively and have found applications in fields as varied as quantum computing, solar power and light-controlled treatment of disease. To best understand how they interact with light, we need to understand what happens when we excite them with light. Therefore in chapter 4, ultrafast polarisation and absorption spectroscopy are applied to one such porphyrin to give a better understanding of the excited state properties and structure.
There are many people that I would like to thank for their support and encouragement throughout the course of my doctoral work. First and foremost I’d like to thank Dr. Olof Johansson for all of his support and guidance over the last three years. His steadfast encouragement and enthusiasm for science were invaluable. I’d also like to thank Prof. Eleanor Campbell, my second supervisor, for her support throughout my PhD.

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Chapter 1

Introduction

Processes within atoms and molecules happen across a wide range of timescales, from phosphorescence, which can take hours, to the motion of electrons between states, which can be as fast as attoseconds ($10^{-18}$ s). As such, there are a wide range of methods for studying an equally wide range of transient phenomena. Manipulation of electrical signals, which underpins many techniques, is only possible for timescales greater than $10^9$ s. In contrast, by using ultrashort ($\sim 10^{-15}$ s) laser pulses, it is possible to use optical spectroscopy to measure changes on ultrafast ($10^{-15} - 10^{-9}$ s) timescales. This is achieved with ultrafast pump-probe spectroscopy, wherein a sample is excited with a "pump" pulse and its properties measured through their effect on a subsequent "probe" pulse. Understanding the response of materials to optical excitation is vital for technologies relying on the interactions between light and matter. Pump-probe optical spectroscopy is one of few methods which can measure effects on ultrashort timescales, making development of improved ultrafast spectroscopy techniques important.

Two of the biggest technologies to which ultrafast spectroscopy is applicable are solar cells, which rely on optical stimulation to generate an electrical potential, and photochemistry, which uses light to drive chemical reactions. Excited states transiently populated by the pump pulse are often much more reactive than their ground state counterparts. If the excited state(s) is occupied long enough that the photoexcited species meets a species with which it can react, then the excited states(s) can drive a reaction.[1–3] Understanding the relaxation pathways of photoexcited materials allows
for better design of efficient, light-driven chemical reactions. While photoexcited states in solar cells do not drive chemical reactions, the motion and separation of charges they cause underpins light-energy conversion technology. Therefore ultrafast spectroscopy can give a better understanding of the process by which carriers are excited and transported throughout the system.[4–6] Both of these technologies are typically studied through changes in the absorption of the probe pulse by the sample.

If the change in polarisation of the probe is measured rather than its intensity, wholly different properties of materials can be probed. The most notable and studied of these is magnetism. The main motivation to controlling magnetisation on ultrafast timescales is for the development of fast and efficient data storage technologies. Magnetic hard drives, which consist of a thin, ferromagnetic film store the majority of the worlds’ data. The film is engineered such that the magnetisation of the magnetic domains in the film can only point in two directions and these therefore encode a 1 or a 0 - a binary bit. Writing a bit requires reversal of the domains magnetisation, achieved by applying a magnetic field using the read/write head. However, this process typically takes nanoseconds. This is significantly slower than the rest of the computer architecture, with typical processor speeds on the order of ~100 GHz, presenting a major bottleneck to increasing computing power.[7] There has therefore been much research on how magnetic systems respond to systems on ultrafast timescales over the past two-and-a-half decades since the initial observations. [8–10]

Measurements of the ultrafast polarisation and intensity change of the probe pulse can clearly tell us a lot about the transient behaviour of a system. As with traditional optical spectroscopy, these properties depend on the wavelength of the probe. Wavelength dependence has long been used to study the properties of materials through static absorption and polarisation spectroscopy, and is common for studying ultrafast absorption change. Broadband transient polarisation change has received much less attention, given that it is typically more difficult to measure. Despite this, it has the potential to give a deeper understanding of transient behaviour and properties. [11–13]

This thesis concerns the development of a setup to measure ultrafast, broadband polarisation change and details its application to several different materials. To put
this work into context, this introduction discusses the theoretical background behind static and then transient magneto-optics and its applications for studying the ultrafast responses of a broad range of materials.

1.1 Magneto-Optics

Magnetic materials are used in a huge range of technologies, from data storage to electric motors, microphones and even childrens toys. As such, fully understanding the behaviour of magnetism in these materials is vital to develop better and more efficient technologies. There are many ways to measure magnetism in a material, from electronic measurements of magneto-resistance to direct measurements of the magnetic field through superconducting quantum interference devices (SQUIDs). However, only optical methods enable the measurement of changes in magnetism on very short timescales ($10^{-15} - 10^{-9}$ s). In all work discussed in this thesis, near ultraviolet (UV) visible and near infrared (NIR) light is used. THz light and X-rays can also be used to measure magneto-optics.[14, 15] but have not been used in this work because of limitations in the laboratory.

Polarised light has an electric field that oscillates in a well-defined direction as the the light propagates. Linear polarisation describes a field oscillating along a single direction, perpendicular to the direction of the travel, with its magnitude changing over
time. In contrast, circular polarisation describes a field that has constant magnitude but whose direction changes over time. As the light propagates, the field rotates about the direction of propagation, while remaining perpendicular to it. The direction of this rotation defines whether the field is left- ($\sigma^+$) or right-handed ($\sigma^-$). Linear and circular polarisation are limiting cases of the more general elliptical polarisation, whose intensity and magnitude varies over time. The field of an elliptically polarised ray of light is shown travelling along the $z$-axis in Fig.1.1. To quantitatively define the polarisation of a photon, the rotation, $\theta$, and ellipticity, $\eta$, are used, and their definitions are shown in Fig.1.1. The rotation describes the direction along which the field is oscillating (although this is undefined for circular polarisation) and the ellipticity how circular these oscillations are (0 for linear and $\pm \pi/2$ for $\sigma^\pm$).

When light is transmitted through a magnetised material, it experiences a change in polarisation through the Faraday effect. Likewise, light reflected off of a magnetisation material also experiences a change in polarisation due to the Kerr effect. Since all experiments detailed in this work were carried out in transmission geometry, I will mainly focus on the Faraday effect here.

Circularly polarised light has an intrinsic angular momentum whose sign reverses upon reversal of the handedness, unlike linearly-polarised light which has momentum, but no angular momentum. Because of this, linearly polarised light can be considered a superposition of equal parts right- and left-handed circular polarisations where the phase difference between the two defines the rotation. This difference in angular momentum leads to different selection rules for different polarisations, and thus they interact differently with materials. Interaction of light with a material is described through the complex refractive index, $N = n + ik$. The real part, $n$, of the refractive index describes the speed at which light propagates through a medium, so if this is different for $\sigma^\pm$ light then a phase difference will be introduced between the two, equivalent to a rotation in the plane of polarisation. For light of angular frequency, $\omega$, the rotation per unit length, $\theta_F$, is given by [16]

$$\theta_F = \frac{\omega}{c} \text{Re}(N_+ - N_-)$$  (1.1)
where \( c \) is the speed of light in a vacuum and \( N_{\pm} \) is the complex refractive index for \( \sigma^\pm \) light. The imaginary part, \( k \), of the complex refractive index describes the attenuation of light by a medium. When \( k \) differs for \( \sigma^\pm \) light then the amount of transmitted \( \sigma^+ \) light will be different to the amount of transmitted \( \sigma^- \) light. If the light incident on the medium is linearly polarised then it will no longer have equal parts \( \sigma^\pm \) light upon exiting the medium, so it will be elliptically polarised. The change in ellipticity per unit length, \( \eta_F \) is therefore

\[
\eta_F = -\frac{\omega}{2c} \text{Im}(N_+ - N_-) \quad (1.2)
\]

which is the imaginary counterpart of Eq.(1.1).

To consider how \( \theta_F \) depends on magnetic fields, the dielectric tensor \( \epsilon \) must be considered rather than \( N \). This describes the response of a system to an applied electric field and is proportional to \( N^2 \). For a cubic crystal (i.e. a system with an intrinsically isotropic dielectric tensor) whose only source of anisotropy is its magnetisation, \( M \), along the \( z \)-direction, \( \epsilon \)

\[
\epsilon(M, \omega) = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
\varepsilon_{xy} & \varepsilon_{xx} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{pmatrix}
\quad (1.3)
\]

where each component is complex: \( \varepsilon_{ij} = \varepsilon_{ij}' + i \varepsilon_{ij}'' \). [17] Since the material is cubic, \( \varepsilon_{xx} = \varepsilon_{yy} \). The off-diagonal components transform antisymmetrically upon reversal of the magnetisation so, to first order, \( \varepsilon_{xy} \propto M \). Relating these components to \( N \) and assuming that \( n >> k \) gives the Faraday rotation and ellipticity

\[
\theta_F(\omega) \approx -\frac{\omega}{2c} \frac{\varepsilon_{xy}''}{n} \quad (1.4)
\]

\[
\eta_F(\omega) \approx -\frac{\omega}{2c} \frac{\varepsilon_{xy}'}{n} \quad (1.5)
\]

Similar relations also exist for the polarisation change of reflected light through the
magneto-optic Kerr effect (MOKE). Importantly for magneto-optics, since both rotation and ellipticity are proportional to $\epsilon_{xy}$, they are therefore also proportional to the magnetic field within the material, providing a direct means through which to optically probe the magnetisation. Since magnetic fields are inherently weak, this approximation holds for almost all cases, except those at very low temperatures and very high fields. Additionally, since $\theta_F$ and $\eta_F$ are proportional to the real and imaginary components of $\epsilon_{xy}$, the Kramers-Kronig relations can be used to calculate one from the other if the whole spectrum is known.[16]

The above derivation is general to any source of anisotropy which might affect the dielectric properties of a material, such as an electric field. The electric equivalent of the Faraday effect is the Pockels effect, where an electric field causes a change in polarisation. Pockels cells utilise this effect to allow for electronic control of polarisation, which can be used to effectively open and close a shutter in nanoseconds, something vital for the function of pulsed lasers. However, while Eq.(1.3) makes no assumptions as to the source of the anisotropy, it does assume that a system is isotropic with no applied field. More detailed and careful derivations of magneto-optical effects avoid this assumption and still find a linear dependence of the Faraday and Kerr effects on the field within the sample, to first order. [18] Furthermore, Eqs.(1.4)–(1.5) assume that a negligible amount of light is transmitted. If this assumption is invalid, then the polarisation change is no longer proportional to the change in $\varepsilon_{xy}$, $\varepsilon_{xx}$ or $\varepsilon_{zz}$ but rather some complex combination of them. In this way the polarisation change is still proportional to the field but does not necessarily correspond to a particular component of the dielectric tensor.

By considering the microscopic meaning of the refractive index, Eq.(1.1) can be thought of more phenomenologically. As linearly polarised light passes through a medium, the electric field of the light causes the electrons in the material to oscillate along the polarisation direction of the light. If the material is magnetised then the oscillating electrons experience a Lorentz force perpendicular to their motion, effectively rotating the direction of oscillations. The oscillating electrons generate light polarised along their direction of motion, so the transmitted light experiences a rotation
of its plane of polarisation. This rotation, \( \theta \), is described through

\[
\theta = VBl
\]

where \( B \) is the magnetic flux density within the sample, \( l \) is the sample thickness and \( V \) is the Verdet constant, which is wavelength and material dependent. This an approximation to first order in \( B \) but it is still only broken in very large fields (\( \sim > 1 \) T) or very low temperatures (\( \sim < 5 \) K) and so the approximation holds for all systems discussed in this work.

Microscopically, the change of ellipticity in a magnetic field is more directly linked to selection rules than rotation. Photons with \( \sigma^\pm \) polarisation have an associated angular momentum \( \pm \hbar \) and because of this, within the dipole approximation, such photons can only cause transitions which change the magnetic quantum number, \( m_j \), by \( \pm 1 \), respectively. Linearly polarised light has no angular momentum so cannot change \( m_j \). With no applied magnetic field, electronic states with different \( m_j \) numbers are usually effectively degenerate for electronic spectroscopy. However, when a magnetic field is applied, the Zeeman effect lifts this degeneracy by an amount proportional to the field (for small fields). Thus transitions from a lower state into states of different \( m_j \) will have different energies. Since \( \sigma^\pm \) light can only increase or decrease \( m_j \), respectively, \( \sigma^\pm \) photons of a given energy will have different probabilities of being absorbed if states with different \( m_j \) are non-degenerate. Therefore more of one circular polarisation will be absorbed than the other so the ellipticity of the light will change.

Magnetic fields are not the only phenomenon which can affect the polarisation of light. Birefringence and other non-linear optical phenomena will also cause polarisation change, a property which is exploited to design wave plates and other polarisation optics. Chirality can also cause a polarisation change in transmitted light in the absence of a magnetic field. Ellipticity and rotation change in this context are typically called circular dichroism (CD) and optical rotary dispersion (ORD). Both can be used as diagnostic tools to identify enantiomers, as a racemic mixture will no longer show CD or ORD. Peaks in CD spectra are much more easily assigned to the corresponding electronic transitions than ORD spectra since ellipticity is more closely linked to the
imaginary component of the dielectric tensor. Because of this, CD is a widely used technique for determination of secondary and tertiary structure in large proteins.[19] Polarisation change of chiral origin will be independent of magnetic field so care must be taken to ensure that these effects are considered when investigating magneto-optics.

Magnetic CD (MCD) and magnetic ORD (MORD) are observed in the presence of a magnetic field and are equivalent to magneto-optical ellipticity and rotation change. As previously discussed, these lift the degeneracy that is usually only broken in the presence of chirality. MCD and MORD typically have features in similar places to their chiral counterparts, but can be measured for a much wider subset of molecules.[20] Especially when their temperature and field dependence is measured, peaks in MCD spectra can provide much more detailed information about electronic structure than absorbance spectra alone.

1.1.1 Interpretation of MCD spectra

In order to leverage quantitative meaning from MCD (ellipticity) spectra, the microscopic origin of ellipticity needs to more carefully be considered. Typically such spectra are measured through the difference in absorption of left- and right handed circularly polarised light in a sample when a magnetic field is applied along the direction of propagation of light. For a transition $|A\rangle \rightarrow |J\rangle$, each with sublevels $\alpha$ and $j$, respectively, the MCD, $\Delta A$, is given by [20]

$$\Delta A = \gamma cl \sum_{\alpha,j} \frac{N_A - N_J}{N_A + N_J} (|m_{-1}^{A,J}|^2 - |m_{+1}^{A,J}|^2) \rho_{A,J}(E)$$

(1.7)

Here $N_A, N_J$ are the populations of the two states. The prefactor $\gamma$ accounts for the effective field correction and various other constants, but its explicit form is unnecessary here as it cancels out later. Concentration and path length are accounted for in the prefactor by $c$ and $l$, respectively. The matrix element accounting for the interaction of the magnetic field is shortened to $m_{\pm 1}^{A,J} = \langle A_{\alpha}|m_{\pm 1}|J_{j}\rangle$. The energy of the light is $E$ and its electric dipole operator is $m_{\pm}$ for $\sigma^{\pm}$ light. Finally, the lineshape of the transition is accounted for with $\rho_{A,J}(E)$, although vibrational levels are neglected here.
for simplicity. The form of Eq.(1.7) is derived using the dipole, Born-Oppenheimer and Frank-Condon approximations.\cite{20} These are valid approximations for the systems and results discussed in this thesis, but still must be considered.

The energies of the states, $E_{\alpha j}$ and their wavefunctions will change upon application of a magnetic field. Assuming that the perturbation is much smaller than the thermal energy this energy shift can be approximated using first order perturbation theory as

$$E'_{A\alpha} = E_{A\alpha} - \langle A\alpha | \hat{\mu}_z | A\alpha \rangle B \quad (1.8)$$

where $B$ is the applied field, $E_{A\alpha}$ is the zero-field energy of the state and sublevel. This is the origin of the Zeeman effect of atomic physics. The magnetic moment operator is given by $\hat{\mu}_z = (\hat{L}_z + 2\hat{S}_z)\mu_B$, where $\mu_B$ is the Bohr magneton and $\hat{L}_z$ and $\hat{S}_z$ are the orbital and spin angular momentum operators along the field direction.

The energies of the states, $E_{\alpha j}$ and their wavefunctions will change upon application of a magnetic field. This shift in energy, $E_Z$, for state $|A\alpha\rangle$ can be approximated using first-order perturbation theory as

$$E_Z = \langle A\alpha | (\hat{L}_z + 2\hat{S}_z) | A\alpha \rangle B = \mu_z B = g_L M_J \mu_B B \quad (1.9)$$

where $B$ is the applied magnetic field and $\hat{L}_z$ and $\hat{S}_z$ are the orbital and spin angular momentum operators, respectively. This is the origin of the Zeeman effect of atomic physics and so $E_Z$ is the Zeeman energy. Evaluating this matrix element gives the second term in Eq.(1.9), where $\mu_z$ is the magnetic moment of $|A\alpha\rangle$. This can instead be written in terms of the total angular momentum quantum number $M_J$, the Bohr magneton, $\mu_B$, and the Landé $g$-factor, $g_L$. The corresponding perturbation to the wavefunctions of $|A\rangle$ and $|J\rangle$ takes into account all the other states, labelled as $|K\rangle$, weighted by $1/(E_K - E_A)$ or $1/(E_K - E_J)$, so only the closest states show significant field-induced mixing. Since the energies of states shift, an applied field will shift the energies of transitions also. It is assumed that the lineshape will have the same shape (i.e. the vibrational sublevels are largely unchanged) but will be shifted in energy to be centred on the new transition energy.
If the energy difference between $|\alpha\rangle$ and $|J\rangle$ is much greater than the thermal energy ($E_J - E_\alpha \gg k_B T$) then the population of $|J\rangle$ is negligible. Here $k_B$ represents the Boltmann constant and $T$ the temperature. Thus the population term in Eq.(1.7) can be simplified to only account for population differences between sublevels of $\alpha$. If $|J\rangle$ is thermally populated then Eq.(1.7) becomes significantly more complicated but it will have the overall effect of reducing $\Delta A$ by an amount proportional to $N_A - N_J$.

Substituting all of the above approximations and expansions into Eq.(1.7) and rearranging gives the expression

$$\Delta A = \gamma B c l \left[ A_1 \left( -\frac{\partial f(E)}{\partial E} \right) + \left( B_0 + \frac{C_0}{k_B T} \right) f(E) \right]$$

(1.10)

where the lineshape $f(E)$ gives the shape of the transition and contains the vibrational information previously contained in $\rho(E)$. The Faraday $A_1, B_0$ and $C_0$ terms are defined as [21]

$$A_1 = -\frac{1}{d_A} \sum_{\alpha,j} \langle J_j | \mu_z | J_j \rangle - \langle A_\alpha | \mu_z | A_\alpha \rangle \left( |m_{A1}^{AJ}|^2 - |m_{A1}^{AJ}|^2 \right)$$

(1.11)

$$B_0 = \frac{2}{d_A} \text{Re} \sum_{\alpha,j,K,K_\kappa} \langle J_j | \mu_z | K_\kappa \rangle \left( |m_{-1}^{AJ}||m_{+1}^{KA}| - |m_{+1}^{AJ}||m_{-1}^{KA}| \right)$$

(1.12)

$$C_0 = -\frac{1}{d_A} \sum_{\alpha,j} \langle A_\alpha | \mu_z | A_\alpha \rangle \left( |m_{-1}^{AJ}|^2 - |m_{+1}^{AJ}|^2 \right)$$

(1.13)

where $d_A$ is the degeneracy of $|A\rangle$. Use of $A_1, B_0$ and $C_0$ groups the terms of $\Delta A$ into the contributions that arise from different sources and have the same lineshape and/or temperature dependence. It should also be noted that Eqs.(1.11)-(1.13) are written using the conventions of Stephens, Piepho and Schatz.[22, 23]

The $A_1$ term has a derivative shape and corresponds to transitions from a non-degenerate ground state to a degenerate excited state whose degeneracy is lifted by the Zeeman effect. A schematic of this is shown in Fig.1.2, where $|J\rangle$ is doubly degenerate. The $|A\rangle \rightarrow |J_{-1}\rangle$ transition will be at lower energy than the $|A\rangle \rightarrow |J_{+1}\rangle$ transition, yet the former is only allowed upon absorption of a $\sigma^-$ photon and the latter $\sigma^+$. Therefore, as the MCD is given by the difference in absorbance of $\sigma^\pm$ light,
Interpretation of MCD spectra

Figure 1.2: Origin of the three terms that make up the MCD spectrum of the $|A\rangle \rightarrow |J\rangle$ transition. The contribution of each term to the MCD is plotted above and the corresponding energy level diagram is shown below. Transitions allowed for $\sigma^\pm$ light are denoted by arrows. The system has no non-magnetic circular dichroism, so when no field is applied (left-most case), no CD is observed.
the difference between two offset absorption peak lineshapes is approximately the first derivative of the lineshape. Crucially, the energy difference between $|A\rangle$ and $|J\rangle$ is much larger than $k_B T$ so all sublevels in $|J\rangle$ are initially unpopulated meaning that occupied $|J\rangle$ states do not need to be taken into account. Because of the derivative in Eq.(1.10)A, this term depends inversely on the bandwidth, $\Delta \Gamma$ of the transition. High-symmetry molecules typically give rise to electronic degeneracies and therefore often show $A_1$ terms.[20] On the other hand, low-symmetry molecules typically have less degenerate electronic states and are therefore much less likely to show $A_1$ terms.

In contrast to $A_1$, the $C_0$ term corresponds to the opposite case: transitions from a degenerate ground state to a non-degenerate excited state. A schematic is shown in Fig.1.2C, where $|A\rangle$ is doubly degenerate. These states will have different energies but the thermal population of the sublevels must be taken into account. The lowest level will always be slightly more populated and, at absolute zero, will be fully populated. Since there is also a shift in energy with field, the $C_0$ term is technically made up of the sum of $f(E)$ and $\frac{\partial f(E)}{\partial E}$, but the former term dominates due to the population difference, hence its form in Eq.(1.10). Here it appears as a positive gaussian, with a small negative tail at the blue end. This term therefore manifests as a feature which scales inversely with temperature. However, at low temperatures and high fields where the Zeeman splitting is much larger than the thermal energy, the lower level will become completely filled so the term will saturate and no longer increase as temperature is reduced. Since it requires a degenerate ground state that is not fully occupied in order to create this population difference, $C_0$ terms will be absent in diamagnetic systems.

The final term, $B_0$, arises from field induced mixing of the states. In the presence of a perturbative field, each states wavefunction will experience a perturbation by all other states, inversely proportional to the difference in energy between them. In the three level system shown in Fig.1.2B, $|K\rangle$ and $|J\rangle$ are relatively near in energy and so the magnetic field causes mixing of these states. This results in a positive peak close to $E_J$ and a negative peak close to $E_K$ whose magnitudes scale with $1/|E_K - E_J|$. If this energy difference is small enough then this will look similar to an $A_1$ term. $B_0$ terms occur in all systems but are only of appreciable magnitude when two states are
Typically, for a broad-band system at room temperature ($g_L = 2, B = 1$ T, $\Delta \Gamma = 10^3$ cm$^{-1}, E_J - E_K = 10^4$ cm$^{-1}, k_B T = 200$ cm$^{-1}$), the approximate relative values of $A_1 : B_0 : C_0$ are 10 : 1 : 50.[20] Therefore, $B$ terms are usually the smallest magnitude terms, but dominate in spectra of low-symmetry species where there is no degeneracy for Zeeman splitting to split.

The definitions for $A_1, B_0$ and $C_0$ in Eqs.(1.11)–(1.13) are not very useful in terms of extracting useful information from the values of $A_1, B_0$ and $C_0$. This is made easier by comparison to the dipole strength of the transition, $D_0$, which itself is given by

$$D_0 = \frac{1}{d_A} \sum_{\alpha,j} \left( |m_{\alpha j}^-|^2 + |m_{\alpha j}^+|^2 \right) \rho_{\alpha j} \quad (1.14)$$

With this, the electric dipole contribution to the Faraday terms can be removed by dividing through by $D_0$. For example, in the case where $S = 0$ and $g_L = 1$, these ratios can be used to determine the $z$-component of magnetic dipole moments through $A_1/D_0 = -\mu_z$(excited state) and $C_1/D_0 = -\mu_z$(ground state).[24] In solution, molecules are randomly oriented and so a factor of 1/3 must be included in Eq.(1.11)-Eq.(1.14) to account for orientational averaging.[23] However, when ratios between $A_1, B_0, C_0$ and $D_0$ are considered, this contribution cancels out.

1.1.2 Jones Calculus

Polarisation of light can be quantified using Jones calculus.[25] This description makes the assumption that the light is fully polarised — depolarised light must be described instead through Mueller calculus. The polarisation of a given ray of light can be considered to be the superposition of a horizontally polarised ray and a vertically polarised ray, or any other pair of orthogonal vectors. Light travelling along the $z$-
direction will therefore have electric field, $E_0$,

$$
E(t) = \begin{pmatrix}
E_x e^{i\phi_x} \\
E_y e^{i\phi_y} \\
0
\end{pmatrix} e^{i(kz-\omega t)} = E_0 \begin{pmatrix}
E_0 e^{i\phi_x} \\
E_0 e^{i\phi_y} \\
0
\end{pmatrix} e^{i(kz-\omega t)}
$$

(1.15)

where $k$ and $\omega$ are the wavevector and angular frequency of the light and $\phi_x, y$ is the phase of the $x$ or $y$ component of the field, respectively. Since $E_z = 0$, the light is completely described by a complex vector with two components for the $x$ and $y$ components, the Jones vector. When light passes through a material, its polarisation and intensity can change. Such effects are described through multiplying the vector by a complex 2x2 matrix. Jones vectors for several common polarisations are given below

Horizontal Linear: $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$  
Vertical Linear: $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$  
$\pm 45^\circ$ Linear: $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$  
$\sigma^\pm$: $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix}$

(1.16)

(1.17)

where all have been normalised and horizontal is deemed to lie along the $x$-axis.

### 1.2 Ultrafast Absorption Spectroscopy

Ultrafast changes to absorption of light rely on a strong understanding of the ground-state, or static, absorption spectra. The absorption of light by molecules in a solution is typically quantified using the Beer-Lambert law

$$
\frac{I}{I_0} = 10^{-A} = 10^{-dC}
$$

(1.18)
Ultrafast Absorption Spectroscopy

Figure 1.3: A schematic of a pump-probe transient absorption experiment. Probe pulses before and after the pump pulse are dispersed onto a detector and the difference between the absorption spectra is recorded. This difference spectrum will be the difference between the decrease in the ground state spectrum and the increase in the excited state.

which defines the absorbance, $A$, in terms of the intensity of light before, $I_0$, and after, $I$, the sample. It also states $A$ is directly proportional to the path length, $l$, concentration, $C$, and extinction coefficient, $\epsilon$, of the sample. The extinction coefficient is wavelength dependent and peaks in absorption spectra can be assigned to particular electronic transitions based on their positions, shapes and relative heights. Transitions which are allowed have greater extinction coefficients than those which are forbidden.

All optical spectroscopy techniques discussed thus far can only measure transitions available to systems in their ground state. In order to observe the properties of excited states, which are typically very short-lived, pump-probe spectroscopy is needed. For this technique, a material is excited with a strong ”pump” pulse of light and then the pump-induced changes are measured through the intensity change of a weaker ”probe” pulse some time afterwards. The difference between the probe spectrum before and after the pump pulse gives the transient absorption (TA). A schematic of this method is shown in Fig.1.3. By measuring the TA for a range of time-delays using ultrashort ($\sim 10^{-15} - 10^{-13}$ s) laser pulses, the response of the system to the pump light can be measured on ultrafast timescales.

In molecular systems, there are three main contributors to the TA signal: ground
state bleach, excited state absorption and stimulated emission. As electrons are excited out of the ground state, its population decreases, resulting in a decrease in absorbance with the same shape as the static spectrum — ground state bleach.[26] Excited state absorption corresponds to the new transitions available to photoexcited electrons and manifests as an increase in absorbance with new peaks corresponding to excited state transitions. Stimulated emission can also sometimes cause a negative TA signal, as the extra emitted light is observed as a decrease in absorbance. Oscillations in the TA are also often observed in response to ultrafast pump pulses and are typically due to vibrational wavepackets. Vibrations modify the interatomic distances and therefore perturb the electronic structure, changing the absorbance at the same frequency as the vibration. [27]

Absorbance is less applicable to crystalline materials, where a non-negligible amount of light may be reflected, so often only the transmittance can be measured. To determine the absorbance of a solid, both reflectance and transmittance must be measured, although they both provide useful information in their own right. Furthermore, the interpretation of transient transmittance (TT) in non-molecular materials is more complex as many additional effects such as free-carrier generation, heating, band gap renormalisation and others may occur.[28–30] Such effects will be discussed in more detail in later chapters, where relevant.

1.3 Ultrafast Magneto-Optics

Ultrafast changes to rotation and ellipticity following stimulation by an intense pump pulse can be measured with pump-probe spectroscopy in a similar manner to TA. Since both are proportional, with caveats, to the magnetic field within the sample, ultrafast polarisation change can therefore be used to probe the magnetic field within a sample, allowing us to measure ultrafast changes to magnetisation. A demagnetisation corresponds to a reduction of the magnetic field within the sample and therefore a decrease in the static MCD or MORD spectrum. This will be measured as a ”ground state bleach” in the transient MCD or MORD spectrum as the strength of the magnetic
Ultrafast Magneto-Optics

Figure 1.4: Ultrafast demagnetisation of nickel, reproduced from Ref.[31]. (a) Remanence following pump pulse, normalised to its value before the pump. Inset are hysteresis loops before and after the pump. (b) Results of three temperature model simulation showing the transient behaviour of the electron, lattice and spin temperatures $T_e$, $T_s$ and $T_l$, respectively.

field within the sample decreases.

This was first achieved in nickel in 1996 by Beaurepaire et al. [31], who observed sub-ps demagnetisation which was orders of magnitude faster than was expected at the time. To ensure that their observed polarisation change was indeed due to a change in magnetisation, they measured the change in the hysteresis loop over time. At room temperature, the hysteresis of a nickel film as measured by MOKE is square but following photoexcitation it was found to become more rounded. Quantifying this as a change in remanent magnetisation they found that the magnetisation rapidly decreased within the first few hundred femtoseconds and then recovering back to its equilibrium value over many picoseconds — see Fig.1.4a. This work opened the door to ultrafast manipulation of magnetisation.

To model their observation of ultrafast demagnetisation, Beaurepaire et al. developed the phenomenological three temperature model (3TM), which considers the transfer of energy between the electrons ($e$), spins ($s$) and lattice ($p$). An effective temperature, $T_i$, can be assigned to each of these reservoirs and their temporal evolution
is described by three coupled differential equations

\[
C_e(T_e) \frac{dT_e}{dt} = -g_{ep}(T_e - T_p) - g_{es}(T_e - T_s) + P(t)
\]

\[
C_s(T_s) \frac{dT_s}{dt} = -g_{es}(T_s - T_e) - g_{sp}(T_s - T_p)
\]

\[
C_p(T_p) \frac{dT_p}{dt} = -g_{ep}(T_p - T_e) - g_{ps}(T_p - T_s)
\]

where \( g_{ij} \) represents the coupling between baths \( i \) and \( j \), \( C_i(T_i) \) their heat capacity and \( P(t) \) the power inputted by the pump pulse. It is assumed that only electrons absorb energy from the pump pulse, which generates a population of hot electrons. Electron-electron scattering between the hot and cold electrons thermalises the electron bath within a few hundred femtoseconds. The electron bath then transfers energy to the lattice through electron-phonon scattering until \( T_e = T_p \), which typically takes several picoseconds. The thermal energy is then dissipated throughout the lattice until both \( T_e \) and \( T_p \) equal the initial temperature of the system. Within this model, the scattering of hot electrons off of phonons and other electrons flips the spins of the electrons. This increases the temperature of the spin bath, which is equivalent to demagnetisation. The demagnetisation therefore begins to recover once \( T_e \approx T_s \), as no more energy is transferred into the spin system from the electrons. The coupling between the baths describes how fast the different subsystems come to equilibrium.

The 3TM describes the demagnetisation of nickel well, as well as many other metallic ferromagnets. However, when the demagnetisation of gadolinium was measured, it did not show the fast initial demagnetisation followed by a slow recovery observed in nickel. Instead, it showed a fast initial demagnetisation followed by a much slower further demagnetisation, which could not be accounted for with the 3TM. The mechanism behind this was suspected to be transfer of angular momentum from the occupied 4f orbitals. To account for this, Koopmans et al. developed the microscopic three temperature model (M3TM), which still uses the electron and lattice temperatures of the 3TM, but includes a derived model for electron-phonon scattering mediated spin-flips...
Figure 1.5: Demagnetisation dynamics of (a) nickel and (b) gadolinium. Electron (red) and phonon (blue) temperatures and magnetisation (green), plotted for typical (c) type I and (d) type II demagnetisation dynamics. Reproduced from Ref.[32].
that describes the change in magnetisation. The M3TM is thus

\[
\begin{align*}
C_e(T_e) \frac{dT_e}{dt} &= \nabla_z(\kappa \nabla_z T_e) + g_{ep}(T_p - T_e) \\
C_p \frac{dT_p}{dt} &= g_{ep}(T_e - T_p) \\
\frac{dm}{dt} &= Rm \frac{T_p}{T_C} \left( 1 - m \coth \left( \frac{m T_C}{T_e} \right) \right)
\end{align*}
\]

where the \( \nabla_z(\kappa \nabla_z T_e) \) term accounts for thermal transport of heat through the system with thermal conductivity \( \kappa \). While the first two equations are similar to Eq.(1.19), the third is markedly different, using the magnetisation relative to its value at absolute zero, \( m \), rather than \( T_s \). In this equation \( T_C \) is the Curie temperature and \( R \) is a material-dependent parameter given by

\[
R = \frac{8a_{sf}g_{ep}k_B T_C^2 V_{at}}{(\mu_{at}/\mu_B)E_D^2}
\]

where \( a_{sf} \) is the probability an electron flips its spin on emission or absorption of a phonon, \( V_{at} \) is the atomic volume, \( E_D \) is the Debye temperature and \( (\mu_{at}/\mu_B) \) is the atomic magnetic moment in units of the Bohr magneton. This model requires no conversion of the magneto-optic measurements into spin temperature and enables measurement of the spin-flip probability \( a_{sf} \), which can also be calculated through \textit{ab initio} methods. Furthermore, it is less empirical and applicable to a much wider range of systems than the 3TM.

Through the M3TM, two broad categories of demagnetisation dynamics were defined: Type I and Type II. The former describes systems like nickel, shown in Fig.1.5a, where the peak demagnetisation occurs before electron-phonon equilibrium is achieved. This results in a fast initial demagnetisation followed by a recovery on the timescale of the electron-phonon equilibration. In contrast, for type II dynamics, the electron and phonon systems come to equilibrium before the spin-system can fully demagnetise. This occurs in gadolinium, shown in Fig.1.5b. The very high peak electron temperature causes a fast initial demagnetisation followed by a slower further demagnetisation as the spin system attempts to come to equilibrium with the now more moderate ele-
tron and phonon temperatures. The greater the chance of an electron-phonon event causing the electrons spin to flip — or larger $a_{sf}$ — the more efficient the demagnetisation process is.

The M3TM is a significant improvement upon the 3TM yet is still relatively simple in its form, so it is the most commonly used model for ultrafast demagnetisation. However, it is not without its problems. To begin with, the temperature of a non-equilibrium population is ill-defined, so it cannot accurately describe dynamics until the electrons have come to equilibrium with each other. Additionally, for demagnetisation to take place, the spin subsystem must lose a large amount of angular momentum and there has been significant debate as to where this angular momentum is transferred. The assumption of the M3TM is that it is transferred to phonons, [32] but ab initio calculations found that transfer of angular momentum to non-equilibrium electrons plays a significant role in the demagnetisation process in nickel. [33–35] More recent experiments on nickel using ultrafast electron diffraction have since shown that non-equilibrium, polarised phonons absorb the angular momentum lost by the spins during the first few hundred femtoseconds.[36] However, in systems other than nickel, there is evidence of many other forms of ultrafast angular momentum transfer driving demagnetisation, such as transfer to magnons [37] or other atoms [38] and even spatial transport through superdiffusive spin currents [39] or spin pumping.[40] The latter two are especially prominent in heterostructures or systems with large spin-orbit coupling.

Demagnetisation is also not the only way in which magnetisation changes on ultrafast timescales, magnetisation can change direction or even increase in magnitude. The former is especially of interest technologically, as it enables ultrafast manipulation of magnetisation. Anisotropy of magnetic materials results in a preferred magnetisation direction, and can arise from crystal structure (magnetocrystalline anisotropy) and the shape of the material (shape anisotropy). This anisotropy most commonly manifests as either an easy-axis, where the magnetisation has a preferred direction, or an easy-plane, where the preferred direction can be any direction within a plane. If the probe, applied magnetic field and easy axis are noncollinear, then the pump-induced change in temperature causes a transient change in the magnetic anisotropy. Because
Figure 1.6: Various examples of ultrafast magnetisation dynamics. (a) Magnetisation precession in a garnet film from Ref.[41] (b) Ultrafast magnetisation reversal in ferrimagnetic GeFeCo from Ref.[42] (c) Demagnetisation of CoPt$_3$ as measured by Faraday rotation and ellipticity, from Ref.[43]
of this, the magnetisation will then precess about its equilibrium easy axis, with the precession amplitude decreasing over time. This results in oscillations in the ultrafast polarisation signal with a frequency that depends on the applied field — typical oscillations for a garnet film are shown in Fig.1.6(a). Precession can be utilised to reverse the magnetisation direction entirely, although this can also be achieved through other ultrafast methods such as using circularly polarised pump pulses or purely thermal methods. Pump pulses can reliably thermally switch the magnetisation in the ferri-magnet GdFeCo. [42] Transient increases in magnetisation have also been observed in the magnetic semiconductors GaMnAs, where the increase in charge carriers was reported to lead to stronger ordering of manganese spins. [44] Significant theoretical work has adapted the M3TM to describe these various processes. [7]

However, as with static spectroscopy, transient polarisation changes can arise through non-magnetic means. The presence of the pump pulse within the sample causes strong non-linearities in the probe when they are overlapped, manifesting as cross-phase modulation (XPM) in TA and TT spectra [45] or the optical Kerr effect (OKE) in transient rotation or ellipticity. [46] Such artefacts do not last longer than the pump and probe durations so have minimal effect on measurements. If excited states have different MCD or MORD spectra to the ground state then this may be observed as a transient signal with the dynamics of the photoexcited carriers. [43] Conversely, a decrease in available carriers in the ground state will cause ground state bleach in the polarisation change. Chiral systems may show an intrinsic CD which can cause transient polarisation change independent of the applied field. Ultrafast CD was used by Oppermann et al. to identify ultrafast conformational changes in Fe(bpy)$_3$ [13] and peptides [47] by deconvoluting the excited- and ground state contributions to the transient CD. Additionally, birefringence can also be caused by the rotation of molecules themselves, showing changes in polarisation as the molecules fall in and out of alignment following perturbation by the pump. [48, 49]

Several transient oscillations were also observed in ultrafast Faraday rotation of a Tb-garnet. [50] These arose from phonon oscillations, electronic coherences between Tb$^{3+}$ sublevels, paramagnetic resonance, and also previously unobserved oscillations
due to the propagation of the pump pulse through the sample. Because of this zoo of effects, while a change in magnetisation will cause a transient change in polarisation, the reverse is not necessarily true — polarisation change alone is not strong enough evidence of a change in direction or magnitude of magnetisation. A change in shape of hysteresis loop [51] or oscillations with a field-dependent frequency [52] are two commonly used methods of identifying demagnetisation. Non-linear optical processes such as second harmonic generation can also be used, taking advantage of the symmetry-breaking nature of magnetisation.[53] Additionally, spectroscopy beyond the visible region, such as THz to probe magnons and phonons directly,[10, 54] or X-rays for element specific transitions, can shed light on ultrafast magnetisation dynamics.[15, 42]

Another, often more accessible, approach is to instead explore the dependence on pump and probe wavelength. Transient changes in absorption and polarisation can vary greatly depending on the probe wavelength used, especially when the system involved is not metallic. Therefore, much more information about the system can be obtained if multiple wavelengths are probed. Carefully choosing probe wavelengths within the visible range meant that Khorsand et al. could achieve element specificity in a TbFe alloy, allowing them to measure the dynamics within each magnetic sublattice — something that is typically done with X-rays. [55] Additionally, by probing either side of the band gap of the ferromagnetic semiconductor EuO, Formisano et al. were able to disentangle the dynamics of short- and long-range magnetic interactions.[11] Tuning the pump wavelength can also aid ultrafast magnetisation manipulation, for example by pumping specific $d - d$ crystal-field transitions to in turn change the magneto-crystalline anisotropy. [54, 56, 57] Since this is a non-thermal method of manipulating magnetisation, it has the advantage of faster and more efficient switching rates. [58]

Much of the research devoted to ultrafast magneto-optics to date has only considered quasi-monochromatic light because of the lack of spectral features in reflectance and transmission spectra of metallic samples. However, much research is now considering alternative materials, such as magneto-plasmonic crystals, [59, 60] molecule-based magnets, [12] and two-dimensional ferromagnets.[61, 62] Along with dielectrics, these materials typically have much richer spectra than metallic materials, providing much
greater scope for wavelength tunability.

1.4 Aims

The overarching aim of this thesis concerns the development of a broadband, ultrafast polarisation spectrometer and its application to a broad range of systems. The development of this spectrometer is detailed in chapter 2, along with its implementation and control systems. Also described are test measurements on several well-studied materials. Chapter 3 details the use of this spectrometer to measure ultrafast magnetisation dynamics in the van der Waals ferromagnet Cr$_2$Ge$_2$Te$_6$ (CGT), which is predicted to have rich magneto-optic properties. By utilising the broadband nature of the spectrometer, the signal can be decomposed into contributions from the demagnetisation and photoexcited electrons to better understand the ultrafast dynamics of the material. Finally, chapter 4 concerns the application of the spectrometer to an organometallic complex, ZnTPP, in solution. Static MCD spectroscopy has been invaluable in determining the electronic structure of this material, so time-resolved MCD could be a way to better understand the excited state structure. Therefore transient MCD spectra are measured with the aim of extracting the excited state MCD spectra.
Chapter 2

Methods

2.1 Ultrafast Pump-Probe Spectroscopy

Pump-probe spectroscopy provides a way to investigate transient changes in materials over ultrafast timescales using ultrashort laser pulses. For changes that occur on timescales of nano- to microseconds these laser pulses are typically generated electronically from a continuous-wave laser through Q-switching and the time-delay between pump and probe pulses controlled electronically. The work described here instead investigates changes on picosecond timescales and so ultrafast laser pulses with a sub-picosecond length must be used. On such timescales, the time-delay cannot be controlled electronically, but can be controlled by adjusting the path length difference between pump and probe pulses.

Generation of ultrashort pulses is achieved using an oscillator. This uses a powerful continuous-wave or nanosecond laser to excite a gain medium such as a titanium doped sapphire. This produces fluorescence which reflects around a cavity forming standing waves. Ultrashort pulses have a much higher peak intensity than continuous waves and so are subject to non-linear optical phenomena such as Kerr lensing, where the refractive index of a medium becomes intensity dependent and causes the beam to self-focus. When the self-focused beam passes through the gain medium, the most intense part is amplified more than the less-intense parts because of the focusing of the pump laser and so the intense part of the beam becomes disproportionately stronger.
By vibrating a mirror, or through other methods, the phase of the fluorescence is randomised. The largest fluctuations in the fluorescence undergo the strongest Kerr lensing and so are amplified the most. Every pass through the gain medium selects for these large fluctuations until eventually all of the energy of the fluorescence is in several pulses. Standing waves form from half-integer numbers of wavelengths so the frequency of these pulses must come from a discrete set. The fourier transform of evenly-spaced Gaussian peaks in the frequency domain is evenly-spaced Gaussian peaks in the temporal domain, which is the equivalent of a sequence of pulses or a pulse train. The same idea applies even to non-Gaussian pulses. The oscillator outputs a sequence of pulses at typical repetition rates of $\sim 100$ MHz and with pulse energies of $\sim 1$ nJ.

For experimental use, stronger pulses are needed than an oscillator can provide. To achieve this, a regenerative amplifier is used to amplify the pulses through chirped pulse amplification. [63] Pulses from an oscillator are first stretched in time using a diffraction grating to delay some frequencies more than others. A single pulse is directed into a cavity where it passes through a laser gain medium that is pumped by a very intense nanosecond laser. With each pass the pulse becomes more and more amplified until an electronically controlled optic, such as a Pockels cell, ejects the pulse from the cavity after a pre-defined delay. The amplified pulse is then compressed to reverse the effect of the stretching and increase the pulse power without changing the pulse energy.

An optical parametric amplifier (OPA) can be used in conjunction with the amplified ultrashort pulses to produce powerful pulses of different wavelengths. Parametric amplification uses a non-linear optical process known as difference frequency generation. This occurs when a strong pump pulse of frequency $\omega_p$ and a second, weaker signal pulse of frequency $\omega_s$ meet inside a non-linear crystal. The signal pulse is amplified while the pump pulse is weakened, and an additional idler pulse, of frequency $\omega_i = \omega_p - \omega_s$, is generated. Maximising the efficiency of this process relies on matching the phase of the initial pulses, typically achieved by rotating the crystal itself. To operate an OPA using a single input pulse, the majority of this pulse is used as the pump pulse and the remainder used to generate the signal. When a femtosecond pulse
propagates through a medium, the light experiences an intensity-dependent refractive index which leads to self-focusing and also to self-phase modulation, which causes small spectral broadening. At the peak of self-focusing in some media, the intensity is such that multi-photon processes change the small spectral broadening into a much wider spectrum - a supercontinuum. A narrow portion of this supercontinuum can then be used as the signal in the difference frequency generation process. Supercontinuum generation can also be achieved in photonic crystals or microstructured fibres where the medium can be tailored for specific spectra,[64] but these are expensive. Bulk media such as sapphire, yttrium aluminium garnet or calcium fluoride are cheaper and can reliably generate supercontinua.

Ultrafast polarisation change provides a means through which to probe additional properties of a material which are inaccessible with absorbance spectroscopy. It is measured using pump-probe techniques where the design of the setup is such that intensity of the light encodes the polarisation change. This can be achieved in several different ways, most of which work for both static and pump-probe methods. The simplest method utilises a polariser and a photodetector after the sample. The probe beam is linearly polarised prior to the sample and the polariser (also called an analyser in this measurement scheme) is aligned such that all light is blocked, acting as so-called crossed polarisers. Therefore any subsequent change in intensity of light reaching the photodetector will be proportional to a change in polarisation of the light. The photodetector is typically a photodiode or a photomultiplier tube, which is more sensitive to very low light levels, connected to a lock-in amplifier or boxcar integrator. Despite its simplicity, this scheme has several disadvantages. It cannot distinguish between a change in rotation and ellipticity of the light, instead measuring their sum in quadrature. Since only intensity is measured and it is minimised initially by the analyser, this exact method only measures the magnitude of the change of polarisation. However, using a nearly crossed analyser can avoid this by allowing the intensity to decrease as well as increase [31]. It can also be circumvented through also using a wave-plate between the two crossed polarisers to introduce a static birefringence. [48] The polarisation change of the sample is then given by subtracting the measured signals for two
equal and opposite birefringence directions. Another disadvantage is that the resultant signal in volts cannot be easily be converted into an absolute change in degrees. This means that the signals measured using different schemes or, importantly, at different wavelengths cannot easily be compared.

Another commonly used method, which overcomes many of the problems with crossed polarisers, is that of balanced photodiodes \([65–67]\). This consists of a Wollaston prism which splits the light into two beams of perpendicular polarisations, the intensities of which are measured by a pair of photodiodes. Rotating a waveplate before the prism until the intensities on the two photodiodes are equal ensures that any subsequent change to the difference in signal across the two photodiodes corresponds to a change in polarisation. Furthermore, unlike crossed polarisers, this method distinguishes between rotation and ellipticity change, resolves the sign of the signal and also allows for conversion to degrees. Since this method forms part of our experimental setup, it will be discussed in more detail in due course.

To detect the signal from a singular photodiode or bridged photodiodes, a lock-in amplifier is typically used, with reference frequency set to the repetition rate of the laser,\([66, 68, 69]\). In the case of continuous-wave lasers, the light is usually modulated using a light chopper prior to detection to improve signal-to-noise. Instead of a lock-in amplifier, the electrical signal from each pulse can be integrated with a box-car integrator,\([49, 70]\), or even computationally using a fast enough analogue-to-digital converter,\([71]\). The latter method can account for shot-to-shot fluctuations in the white-light continuum by comparing the energies of individual pulses.

However, a major limitation of both the crossed polarisers and balanced photodiodes methods is that they can only measure a single wavelength at once. Both measurement schemes can be used for both static and pump-probe spectroscopy, but here the focus will be on the latter. Sources of UV, visible or infrared probe light for both methods are typically the fundamental or second harmonic of an ultrafast laser or the output of an OPA, since both provide intense and stable light,\([55, 72]\). A small section of a supercontinuum can also be used as a less stable but more flexible alternative, and a spectrum can be slowly measured one wavelength at a time,\([12]\).
the whole spectrum at once is much more efficient, and is done in many commercial static spectrometers. It can be achieved in a time-resolved manner by spectrally dispersing a white-light supercontinuum onto a CCD array. Combining such a technique with various polarisation optics enables measurement of polarisation change across the spectrum. [73, 74] The sample and the polarisation optics never affect polarisation in a completely achromatic manner, so care must be taken when measuring the spectrally resolved polarisation change. Due to this, to measure ellipticity spectra, both Bigot et al. and Richter et al. first recorded the magneto-optical spectrum as function of analyser angle and then extracted the true polarisation change. However, these additional measurements add greatly to the total measurement time.

Alternatively, the ellipticity change can instead be recovered by measuring the absorption of left- and right-handed circularly polarised light. Ellipticity spectra measured this way are typically called magnetic circular dichroism (MCD) spectra.[72, 75] Typically, MCD spectra are measured by rapidly changing the handedness of the light incident on the sample through the use of a photoelastic modulator.[76] However photoelastic modulators limit one to measuring a narrower wavelength range, and they reverse polarisation at a much faster rate than the repetition rate of our laser. [47] Instead of reversing the handedness of the light, one can reverse the direction of the applied magnetic field. [77] This approach is especially applicable to non-visible light, where photoelastic modulators may not be available. For example, low energy X-rays can be generated through high-harmonic generation in a benchtop setup and used with this method to measure X-ray MCD spectra. [78] Pump-probe measurements are achieved through this setup by measuring the transient absorbance for opposing field directions, so this can be adapted from an existing transient absorbance spectrometer.

White-light supercontinua typically show strong temporal and spectral noise correlations [45, 64] so care must be taken to reduce these. Broadband transient absorbance spectrometers make frequent use of supercontinuum probe beams and can achieve shot-noise limited spectra. [79] This is typically achieved through simultaneously measuring the spectrum of a reference beam to make use of shot-to-shot referencing and thereby account for fluctuations in intensity across the spectrum. Noise can also be reduced
Chapter 2.2.1

2.2 Experimental Setup

2.2.1 Broadband CCDs

This chapter is adapted from a published manuscript: Ref.[84]. The spectrometer from which this setup was developed is described in Ref. [27] and it based on the one described in Ref. [85]. An amplified Ti:Sapphire laser system produces 120 fs pulses of 800 nm light at a repetition rate of 1 kHz (top-left of Fig. 2.1). A 90/10 beam splitter (BS1) is used to separate out the pump and probe pulses. Since the publication of Ref.[84], a new laser (Light Conversion PHAROS) was installed which produces 1030 nm, 270 fs pulses at a user-defined repetition rate of < 25 kHz, or up to 200 kHz at lower pulse energy. In addition, half of the light from the Pharos is used to pump an non-collinear optical parametric amplifier (NOPA, Light Conversion...
ORPHEUS). This produces 70 fs pulses in the range 660-940 nm with the signal beam and 1100-3000 nm with the idler beam. A second harmonic generation stage (Light Conversion Lyra) is also used to double the signal beam into the range 330-470 nm. The remaining 1030 nm beam from the Pharos is used to generate a supercontinuum for probing the sample and the NOPA used as a pump. Aside from this change to the origin of the beams and with mirrors in different places, the rest of the setup is functionally the same.

The pump beam is initially attenuated with a graduated neutral density filter (ND2). When both pump and probe are generated from 800 nm pulses, a beta barium borate (BBO) crystal can be used to frequency-double the pump pulse and the remaining 800 nm light filtered out. A chopper blocks every second pulse before the light is directed into a motorised delay stage (Aerotech PRO225LM), which introduces a controllable time delay. Half- or quarter-wave plates can be introduced here to manipulate the polarisation direction of the pump. The pump beam is focused onto the sample using a 50 cm focal length spherical mirror. An aperture (AP2) centred on the probe beam is used to block the residual pump beam after the sample and a linear polariser (LP3) can be inserted perpendicular to the polarisation of the pump beam to further reduce the amount of scattered pump light from the sample.

In order to achieve broadband measurements, a broadband probe pulse is needed. The probe beam passes through a half-wave plate (HWP1) and polariser (LP1), an aperture (AP2), and a lens which optimise the beam for generation of a white-light supercontinuum in a CaF$_2$ or sapphire plate. For white light generation with 800 nm pump, a neutral density filter was used to attenuate the light instead of the half-wave plate and polariser. CaF$_2$ produce a very broad spectrum from around 330 nm to at least 750 nm, since the remaining 800 nm light is removed by a 750 nm shortpass filter. The intensity decreases greatly below 400 nm, the light is unstable above approximately 650 nm and the plate must also be constantly moved to prevent damage to it. While the CaF$_2$ has a broad spectrum, it is noisier and moves slightly (tens of microns) as the plate is translated. In contrast, a supercontinuum generated in sapphire ranges only from about 490-750 nm but is much more stable and sapphire much less easily damaged.
Figure 2.2: Spectra of the probe and reference beams generated in CaF$_2$ and Sapphire plates by (A) 800 and (C) 1030 nm light, respectively. The standard deviations of the spectra are plotted in (B,D), and are given as a percentage of the corresponding spectra in (A,C), respectively.
In addition, the durability of sapphire means that white light can be generated at a repetition rate of up to 20 kHz. The spectrum of the light generated in the two media depends also on the fundamental wavelength, as well as the optics the light meets before detection. Optimal spectra of the supercontinuum from the two media generated with 800 nm light are plotted in Fig.2.2(A), where the spectra measured by the probe and reference camera are both shown. The spectra shown here are plotted against the pixel number of the CCD rather than wavelength, but 0 and 500 correspond to roughly 350 and 750 nm. Due to the different optics used in the probe and reference lines, there is a clear difference between the two, especially towards the blue end of the spectrum. The difference in range of the two media can also be very clearly seen, and the sudden drop above pixel 500 is caused by the 750 nm shortpass filter. Fig.2.2(B) shows the standard deviation of the spectra in (A) as a percentage. For a very well optimised probe beam, these are well below 1%. For comparison, the equivalent spectra but generated with 1030 nm light are plotted in (C). The ranges of the spectra are similar to (A) but the sapphire light is slightly narrower, only reaching 490 nm, as opposed to 470 nm in CaF$_2$. Both spectra are also much weaker above 700 nm, even though the same filter is used. Care was taken to use the same optics between probe and reference lines when building the new setup so, importantly, [79] the probe and reference spectra are much closer to one another. The corresponding standard deviations are plotted in Fig.2.2. All are below 1% but the sapphire spectrum is more stable, with a noise of around 0.1-0.2% around its maximum intensity, compared to 0.4-0.5% for the CaF$_2$. The large peak in the standard deviation of the sapphire light corresponds to the high energy edge of the spectrum below pixel 400 nm. Furthermore, since the CaF$_2$ is easily damaged and this increases the noise of the spectrum over time. All spectra in Fig.2.2 were recorded with no polarisation optics after supercontinuum generation. However, addition of wave-plates can reduce the UV intensity and polarisers make the signal noiser, both of which have a greater effect on the CaF$_2$.

The linearly polarised probe pulses can be circularly polarised using an achromatic quarter-wave plate (QWP1: Thorlabs AQWP05M-600). For CaF$_2$ light, the low transmittance of the QWP below 400 nm removes most of the already low-intensity UV part
of supercontinuum, reducing the range to around 400 − 650 nm. However, QWP1 can be substituted for one more suitable for the UV so that wavelengths down to 300 nm can be investigated, albeit at the cost of a much reduced range at longer wavelengths. To generate a reference signal, a beam splitter (BS2) diverts half of the beam towards the detection stage. The probe beam is focused using a 50 cm focal length spherical mirror through the poles of the electromagnet onto the sample, where it overlaps with the pump beam. The angle between the pump and probe beams is 1.2° and their $1/e^2$ beam widths at the sample are around 110 and 65 µm, respectively. By aligning the probe beam with holes drilled through the poles of the magnet, both the probe and magnetic field are normal to the sample.

To measure the width of these beams and also observe their quality, a mirror is placed before the electromagnet to divert the beam into a CMOS camera at the focus. The probe and pump beams are attenuated with ND filters first so as to not saturate the camera. The images of the beams are then fit to a 2D gaussian in MATLAB and the average width is taken as the beam waist. Since the supercontinuum diverges from the nonlinear medium, a spherical mirror directly after the medium is used to collimate the beam. The probe beam should look circular and roughly gaussian and a poorly collimated beam will instead be elliptical. Therefore the position of the collimation
mirror is adjusted by observing the beam through the CMOS camera, after using a bandpass filter to select a narrow bandwidth. Typical profiles of the 800nm pump and 1030 nm-generated sapphire white light probe beams, as measured by the CMOS camera, are shown in Fig.2.3.

After the sample, the probe beam is then directed through a UV fused silica prism (Eksma Optics 320-1218) and focused onto a CCD (Entwicklungsbüro G. Stresing, Double Line Spectrometer system with Hamamatsu S7030-0906 sensors), identical to that which measures the spectrum of the reference beam. These two CCD arrays each consist of 512x128 pixels, which measure the light incident on them each millisecond, and have a resolution of approximately 0.7 nm per pixel. To calibrate which pixel corresponds to which wavelength, a spectral filter (Fcal:Thorlabs FGB67M) with a rich and detailed spectrum is inserted into the beam. This also ensures that the same pixels on the reference and probe CCDs correspond to the same wavelengths. A LabVIEW program controls the setup and handles all processing, such subtracting pump-on from pump-off spectra, in real-time so that the TA and TRMCD spectra are saved at the end of the measurement. The chirp of the white-light continuum is corrected for at the
end of the measurement by finding the time-delay at the centre of the initial rise (or of the cross-phase modulation, if present) manually for 10 – 20 wavelengths. This is then fit to a third order polynomial and the TA and TRMCD spectra are interpolated to remove the wavelength-dependence of time-zero.

The sample is placed between the poles of a 0.4 T electromagnet (GMW 3470) with 10 mm diameter axial holes in the poles. To achieve a 0.4 T field, a current of 5 A is applied by a unipolar power supply (Aim-TTi CPX400SP). In order to reverse the field, the supply is turned off, the current direction reversed and then turned back on. A cryostat can also be placed in the sample position to carry out low temperature measurements.

Manual reversal of the magnetic field is inefficient and makes experiments take much longer than necessary. Therefore, to further automate experiments, an automatic switch was developed to make switching faster. It consists of two relay switches controlled by an Arduino board, and a circuit diagram of this is shown in Fig.2.5. When no voltage is applied to the two switches, current flows from the power supply to the magnet. To reverse the current direction, a LabVIEW subVI turns off the output of the power supply, tells the Arduino to output a voltage to both switches, changing the switch from NC to NO or vice versa, and then turns the power supply output back
on. Failsafes are included in the LabVIEW code to turn off the output if the arduino fails.

2.2.2 Static Faraday Rotation

The rotation of light caused by the sample in a magnetic field is measured using a polariser after the sample (LP3 in Fig. 2.1). QWP1 is not used in this configuration. The linearly polarised white-light supercontinuum passes through the sample, the polariser and is subsequently dispersed onto the CCD to measure its spectrum. As described previously, Jones calculus can be used to quantify the effect of the polariser angle and the sample itself on the measured spectrum. Light incident on the sample is horizontally polarised and described by the vector \( |p\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \). As with the bridged photodiodes, it is assumed that the effect of the sample on the light itself is given by

\[
W = \begin{pmatrix} 1 & \Theta \\ -\Theta & 1 \end{pmatrix},
\]

(2.1)

where \( \Theta = \theta - i\eta \). Here \( \theta \) and \( \eta \) denote the rotation and ellipticity induced by the sample, respectively. However, \( \theta \) and \( \eta \) only correspond to the actual change in polarisation state when \( |\Theta| \ll 1 \) rad (\( \sim 57 \) deg). The maximum signal observed throughout this work is \( \sim 750 \) mdeg, which is well within this threshold. It is assumed that \( \Theta \) is proportional to the magnetic field within the sample and so reversal of the applied field changes the signs of the off-diagonal terms in \( W \). The field within the sample depends on both the applied field and the magnetisation of the sample and so the rotation will not necessarily scale linearly with the field. However, unless the critical field of the sample is far above 0.4 T, reversal of the applied magnetic field will reverse the field within the sample and therefore the sign on \( \Theta \).

After transmission through the sample, the light passes through LP3, whose effect
on the light is described by

\[ P = \begin{pmatrix} \cos^2 \beta & \cos \beta \sin \beta \\ \cos \beta \sin \beta & \sin^2 \beta \end{pmatrix}, \quad (2.2) \]

where \( \beta \) is the angle that the polariser’s axis of transmission makes to the horizontal plane. The light reaching the CCDs is denoted \( |p'\rangle = PW |p\rangle \) and the measured intensity at the CCDs, \( S \), is given by

\[ S = \langle p'|p' \rangle. \quad (2.3) \]

In the setup described in Fig. 2.1, two CCDs record the intensity of the probe and reference beams simultaneously. The transmittance, \( T \), of the sample is given by the ratio of the intensity of transmitted light to the light’s incoming intensity and is converted to absorbance through \( A = - \log_{10} T \). This conversion neglects any light which has been reflected or scattered and so the absorbance only corresponds to absorbed light when there is negligible reflection or scattering. Furthermore, the probe and reference beams travel different paths to their detectors, and so have slightly different spectra. Thus, while the reference beam is valuable for tracking and reducing fluctuations of the probe intensity, it cannot be reliably used as an accurate representation of the probe beam incident on the sample. Only the ratio of \( T \) before and after the magnetisation reversal (or pump pulse) is relevant, so slight changes in spectra and non-negligible reflectance can be ignored, since these cancel out when the ratio is calculated.

The probe beam passes through the sample and its intensity in the presence of a positive or negative magnetic field, \( S^\pm \), is given by Eq.(2.3). Although the reference beam is unaffected by the sample, it is still subject to fluctuations in the supercontinuum generation so the reference intensities corresponding to \( S^\pm \) are denoted \( R^\pm \). The change in absorbance between positive and negative fields, \( \Delta A \), can therefore be
expressed as
\[ \Delta A = A^+ - A^- = -\log_{10} \left( \frac{S^+ R^-}{R^+ S^-} \right), \] (2.4)

Since the ratio \( R^-/R^+ \) only accounts for fluctuations in the intensity of the light, it is assumed that \( R^-/R^+ = 1 \), which simplifies the subsequent calculations. Substituting Eqs. ((2.1)) – ((2.3)) into Eq.(2.4), it is found that
\[ \Delta A = -\log_{10} \left( \frac{\cos^2 \beta + \sin^2 \beta |\Theta|^2 - 2\theta \sin 2\beta}{\cos^2 \beta + \sin^2 \beta |\Theta|^2 + 2\theta \sin 2\beta} \right), \] (2.5)

where \( \Delta A = 0 \) if the polariser is parallel or perpendicular to the incoming light. However, when the polariser is intermediate at \( \beta = \pi/4 \), then \( \Delta A \approx (4/\ln 10) \theta \) provided that \(|\Theta| << 1\). This is therefore a means through which we can measure Faraday rotation or, equivalently, the magnetic optical rotatory dispersion (MORD) spectrum.

To measure a static spectrum, \( S^+ \) and \( R^+ \) are recorded over a large number of laser pulses (typically 3000, which takes three seconds per acquisition given the 1 kHz repetition rate) and then \( S^+ / R^+ \) is averaged. When the field is reversed, \( S^- / R^- \) is obtained in the same manner so that Eq.(2.4) can be used to calculate the MORD spectrum. This is repeated as necessary, and we find that the sensitivity of static MORD (and MCD) is typically limited to around 5 – 10 mdeg, although additional averaging can reduce this further. This noise level is larger than that of typical static MCD spectrometers due to the high inherent noise level of femtosecond supercontinuua.

\[ \text{2.2.3 Static Faraday Ellipticity} \]

If LP3 is removed and a quarter-wave plate (QWP1) inserted before the sample, ellipticity rather than rotation can be measured. Light circularly-polarised by QWP1 passes through the sample in the magnetic field and is then dispersed onto the CCD. In the same procedure as with the rotation measurements described above, the change in absorbance between positive and negative applied fields gives the ellipticity. The phase difference for light travelling along the perpendicular fast- and slow-axes of a wave plate is given by its retardance, \( \rho \). For a half-wave plate, which rotates the plane of polarisation of linearly polarised light, \( \rho = \pi \). Quater-wave plates can convert linearly to
circularly polarised light, and so require that $\rho = \pi/2$. To ensure that measurements can be carried out at a wide range of wavelengths, QWP1 must be achromatic such that all wavelengths have the same polarisation. No wave plate is truly achromatic, but if its retardance is known then its effect on the ellipticity can be calculated. The effect of the quarter-wave plate is therefore quantified as [86]

$$Q = e^{i\rho/2} \begin{pmatrix} \cos^2 \alpha + e^{i\rho} \sin^2 \alpha & (1 - e^{i\rho}) \sin \alpha \cos \alpha \\ (1 - e^{i\rho}) \sin \alpha \cos \alpha & \sin^2 \alpha + e^{i\rho} \cos^2 \alpha \end{pmatrix}.$$  (2.6)

where $\alpha$ is angle between the fast axis of the waveplate and horizontal axis of the laboratory frame. The light reaching the CCD is denoted $|p'\rangle = QW|p\rangle$. From substituting this into Eq.(2.3) and simplifying, the intensity of the light in the presence of positive and negative fields is given by

$$S^\pm = 1 + |\Theta|^2 \pm 2\eta \sin 2\alpha \sin \rho.$$  (2.7)

Since the change in rotation and ellipticity is small, $|\Theta| << 1$ rad, the total change in absorbance can be approximated from Eq.(2.4) as

$$\Delta A \approx -\frac{4}{\ln 10} \eta \sin 2\alpha \sin \rho.$$  (2.8)

Therefore, $\Delta A$ is proportional to the ellipticity. This proportionality is more clear if $\alpha = \pi/4$ and $\rho = \pi/2$. Converting $\eta$ to degrees and assuming a perfect wave plate, gives the result that

$$\eta[\text{degrees}] \approx 33\Delta A[\text{OD}].$$  (2.9)

The MCD can also be measured by directly measuring the change in absorbance of left- and right-handed circularly polarised light in a constant magnetic field. In this case the conversion between absorbance change and ellipticity can be calculated by
considering the definition of ellipticity [20] in
\[
\tan \eta = \frac{E_{RHC} - E_{LHC}}{E_{RHC} + E_{LHC}} = \frac{\sqrt{I_{RHC}} - \sqrt{I_{LHC}}}{\sqrt{I_{RHC}} + \sqrt{I_{LHC}}}
\] (2.10)

where \(E_{RHC/LHC}\) and \(I_{RHC/LHC}\) is the electric field and intensity of the right- and left-handed components. Using the Beer-Lambert law and assuming \(\eta \ll 1\) gives
\[
\eta[\text{radians}] \approx e^{\Delta A \ln 10/2} - 1 \over e^{\Delta A \ln 10/2} + 1
\] (2.11)

where \(\Delta A = A_{RHC} - A_{LHC}\) is the difference in absorbance for right and left handed circularly polarised light. Assuming that the absorbance change is small, \(\Delta A \ll 1\), and converting from radians reduces this to
\[
\eta[\text{degrees}] = \Delta A \frac{\ln 10 \times 180}{\pi} \approx 33\Delta A[\text{OD}].
\] (2.12)

This is identical to Eq.(2.9) even though it is derived from a different equation, showing the equivalence between reversing the field and reversing the handedness of the light for MCD signals.

If the wave plate is imperfect, then the effect of the wavelength-dependent retardance can be removed from the measured MCD spectrum by dividing by \(\sin \rho\). The retardance of QWP1, as recorded by ThorLabs, varies by at most 20% from its ideal value of \(\pi/2\) rad. From Eq.(2.8), this reduces the measured MCD spectrum by 5% at most, so the retardance of the wave plate has a minimal impact on the measurements. The bridged photodiodes are used with a 460 nm bandpass filter to ensure that QWP1 is at the correct angle to circularly polarise the probe beam. If the waveplate is misaligned then its achromatic retardance has a more disruptive effect on the measured ellipticity.
2.3 Time-Resolved Measurements

2.3.1 Broadband CCDs

To record time-resolved changes in absorbance, the difference between the steady-state absorbance spectrum, $A_0$, and the spectrum at time delay $t$ following a pump pulse, $A(t)$, is measured. By blocking every second pump pulse, the difference between adjacent shots gives the transient absorbance. Reference spectra are measured simultaneously alongside every laser shot. The TRMCD in degrees, $\Delta A_{MCD}(t)$, is therefore given by

$$\Delta A_{MCD}(t) = \left[ (A^+(t) - A^-(t)) - (A_0^+ - A_0^-) \right]$$

$$= -\log_{10} \left( \frac{S^+(t)R^-(t)R_0^+S_0^-}{R^+(t)S^-(t)S_0^+R_0^-} \right)$$

$$\approx \frac{1}{33} (\eta(t) - \eta_0) \quad (2.13)$$

using the same notation as with the static MCD, Eq.(2.4). Experimentally, a transient absorbance spectrum is measured for each field direction with circularly polarised light, and the difference in absorbance between the two is found. As with the static spectra, the inclusion of the reference spectra in Eq.(2.13) greatly improves the sensitivity of the time-resolved spectra. Typically, each delay point is averaged over 2000 consecutive pulses, resulting in a sensitivity of 1 mdeg, due to the shot-to-shot and spectral referencing. This value can be decreased to 0.4 mdeg when averaging over a narrow spectral range, as discussed below. This sensitivity is of the same order of magnitude as the sensitivities of other broadband (magnetic) circular dichroism spectrometers. [47, 75, 87] Instruments with higher sensitivities use much longer integration times [88] (several minutes) or use an OPA as an intense and stable light source to only probe one wavelength at a time. [72]

If a sample does induce transient changes to the polarisation state of the transmitted light, then $S^+ \neq S^-$. Therefore, to recover the TA spectrum, $\Delta A_{TA}(t)$, the average of
the spectra measured in opposing fields is taken. This modifies Eq.(2.13) to:

\[ \Delta A_{TA}(t) = \left[ (A^+(t) + A^-(t)) - (A^+_0 + A^-_0) \right] / 2. \]  

(2.14)

This means that both the TA and TRMCD are measured simultaneously.

Time-resolved changes in the Faraday rotation spectrum can also be measured with Eq.(2.13) once the setup is rearranged into the same geometry used for the static rotation measurements. Since the polariser cuts out half of the light, rotation measurements are slightly less sensitive than ellipticity measurements.

Solid samples often reflect a non-negligible amount of light and so the transmittance does not necessarily correspond to absorbance. Therefore, transmittance change is used instead of absorbance change for such samples. Approximating a constant reference signal, the transient change in absorbance is given by

\[ \Delta A(t) = -\log_{10} \left( \frac{S^*(t)}{S^0(t)} \right) = \log_{10} \left( \frac{S^*(t) - S^0(t)}{S^0(t)} + 1 \right) \]  

(2.15)

The proportional change in transmittance, \( \frac{\Delta T}{T} = \frac{S^*(t) - S^0(t)}{S^0(t)} \), is much smaller than one for all cases discussed here. Therefore, Eq.(2.15) can safely be approximated and rearranged to

\[ \frac{\Delta T(t)}{T} \% = -100 \ln(10) \Delta A(t) \]  

(2.16)

The percentage change in transmittance is found from \( \Delta A \) through a simple multiplicative factor.

For pump-probe measurements, pump light scattered by the sample often dominates at wavelengths close to the pump wavelength in the resulting spectrum. The ideal method of removing this scatter light is the use of a filter which blocks the pump but allows the rest of the probe to pass unhindered. However, this is often not possible, especially if the pump wavelength is within the probe supercontinuum. Another option in regular TA spectra is to use a linear polariser. If the pump and probe are both linearly polarised with perpendicular planes of polarisation, the polariser can be placed after the sample and adjusted so that all the pump light is blocked while not affecting
the probe. Of course, care has to be taken to avoid optical anisotropy effects, but there are ways around this. [89] With careful consideration of the angles, it is possible to use the polariser to remove scattered light even when measuring MCD spectra. In order to investigate how this impacts the ellipticity measurements, the Jones vector description detailed above is used again.

The light reaching the CCDs is now given by $|p'\rangle = PWQ |p\rangle$. Substituting this into Eqs. ((2.3)) – ((2.4)), under the assumption that $|\Theta| << 1$, it is found that

$$\Delta A \approx \frac{4}{\ln 10} \frac{\theta \sin 2\beta \cos \rho + \eta \sin \rho}{1 + \cos \rho \cos 2\beta}$$

$$= \frac{4}{\ln 10} \frac{\eta \sin \rho}{1 + \cos \rho} \quad \text{for } \beta = 0$$

When the polariser is parallel or perpendicular ($\beta = 0$ or $\pi/2$) to the incoming light, then $\Delta A$ is proportional to $\eta$ but is much more dependent on the retardance of the wave plate than Eq.(2.8). If the polariser angle is intermediate between these, then $\Delta A$ depends not only on $\eta$ but also $\theta$. To remove pump scatter when a filter is unavailable, we set $\beta = 0$. A polariser can therefore be used to remove pump scatter, although the effects of the imperfect retardance of the quarter-wave plate can no longer be ignored and the results must be corrected for this. Furthermore, the intensity of the light reaching the CCD is approximately halved by the polariser, which decreases the sensitivity of the spectrometer compared to time-resolved measurements that exclude the polariser.

### 2.3.2 Bridged Photodiodes

In some situations, a monochromatic polarisation detection scheme is preferable and it also allows comparisons between different measurement methods. A pair of bridged photodiodes (Thorlabs PDB210A/M) used in conjunction with a lock-in amplifier (Zurich Instruments MFLI) provide another method of measuring femtosecond magneto-optics. The setup used for this is shown in Fig.2.6. The bridged photodiodes (PDs) are used rather than two single PDs because the bridged PDs have three outputs: two of which output the signal from each PD and another which outputs the difference in signal
between the two PDs. This difference signal is typically very small and so it is amplified in a noise-sensitive manner through electronics in the bridged PDs. Probe pulses are focused onto the PDs to ensure that the beam is smaller than the detector area. This means that all of the beam hits the PDs and it is tolerant to small deviations of the beam that could be caused by a transient change to refractive index [90]. A (quasi-)monochromatic beam is directed into a Wollaston prism (WP) which splits the beam into perpendicular polarisation components that are detected with the two PDs. The lock-in amplifier with a reference frequency set to the repetition rate of the laser then detects the difference in signal between the two PDs.

The rotation of light through the sample can be measured using a half-wave plate (HWP2) directly before the photodiodes. Horizontally polarised light, represented by $|p\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, passes through the sample then through a half-wave plate at angle $\gamma$ to the horizontal before being split by a Wollaston prism. The state the light reaching the
Wollaston prism, $|p'\rangle$, is therefore

$$|p'\rangle = \mathbf{H}(\gamma)\mathbf{S}|p\rangle$$  \hspace{1cm} (2.18)

$$\begin{pmatrix} \cos(2\gamma) & \sin(2\gamma) \\ \sin(2\gamma) & -\cos(2\gamma) \end{pmatrix} \begin{pmatrix} 1 & \Theta \\ -\Theta & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$  \hspace{1cm} (2.19)

where $\Theta = \theta - i\eta$ describes the rotation and ellipticity of the sample (provided that $|\Theta|^2 << 1$). The signal measured by the photodiodes is proportional to the difference in intensity of the two components of $|p'\rangle$. Therefore, the intensity difference, $\Delta I$, is given by

$$\Delta I = \langle p'\rangle \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} |p\rangle = \cos(4\gamma)(1 - |\Theta|^2) - 2\theta \sin(4\gamma) \approx \cos(4\gamma) - 2\theta \sin(4\gamma)$$  \hspace{1cm} (2.20)

At the beginning of each measurement, the PDs are ”balanced” by rotating the wave-plate to minimise $\Delta I$. Since $|\Theta|^2 << 1$, the value of $\gamma$ at which the signal is minimised is typically very close to one where $\cos(4\gamma) = 0$ and therefore $\sin(4\gamma) \approx 1$. This reduces Eq.(2.20) to $\Delta I \approx -2\theta$ so changes to rotation are therefore proportional to changes in difference in intensity. To convert from the voltage measured by the PDs, $\Delta V$, into a rotation in radians, the total intensity hitting the PDs must be known. This is measured by blocking one balanced PD and measuring the difference in signal between the two PDs, $V_0$, which must now correspond to half the total intensity. The rotation in radians is therefore given by

$$\theta[\text{rad}] = \frac{\Delta V}{4V_0}$$  \hspace{1cm} (2.21)

A change in ellipticity can be measured similarly to the rotation by using a quarter-wave plate (QWP2) in front of HWP2. In this case, the vector of the light at the
Bridged Photodiodes

Wollaston prism is

$$|p'⟩ = H(γ)Q(α)S|p⟩$$  \hspace{1cm} (2.22)

$$= \begin{pmatrix} \cos(2γ) & \sin(2γ) \\ \sin(2γ) & -\cos(2γ) \end{pmatrix} \begin{pmatrix} \cos^2(α) + i\sin^2(α) & (1 - i)\cos(α)\sin(α) \\ (1 - i)\cos(α)\sin(α) & \sin^2(α) + i\cos^2(α) \end{pmatrix} \begin{pmatrix} 1 & Θ \\ -Θ & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$  \hspace{1cm} (2.23)

where the angle of the fast axis of QWP2 to the horizontal is defined as α and the same $|Θ|^2<<1$ condition applies. The difference signal measured by the photodiodes is given by

$$ΔI = ⟨p'| \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} |p⟩$$ \hspace{1cm} (2.24)

$$= \cos 2α [\cos(2α)\cos(4γ) + \sin(2α)\sin(4γ)] (1 - |Θ|^2) - 2θ \sin(2α) [\cos(2α)\cos(4γ) + \sin(2α)\sin(4γ)] + 2η [\sin(2α)\cos(4γ) - \cos(2α)\sin(4γ)]$$  \hspace{1cm} (2.25)

The photodiodes are balanced first by removing QWP2 and rotating HWP2 to minimise $ΔI$, then QWP2 is reinserted and rotated to minimise $ΔI$ again. For $|Θ|^2<<1$, this procedure results in $\cos(4γ) \approx 0$ and $\sin(2α) \approx 0$, which reduces Eq.(2.25) to $ΔI \propto -2η$ and this is converted to radians also through Eq.(2.21).

For static magneto-optics, a continuous wave 450 nm diode laser (ThorLabs CPS450) can also be used. The laser is modulated by a chopper, attenuated using an ND filter and directed into the probe line of the sample where it is focused onto the sample by a spherical mirror, resulting in a $1/e^2$ beam waist of $\sim 60 \text{µm}$. After this, it is directed into the photodiodes and then detected by the lock-in amplifier at the frequency of the chopper. Despite being limited to continuous wave at a single wavelength, the diode laser is much more intense and stable than the white-light continuum. Therefore, the diode laser is often used for measurements of magnetic hysteresis.

For measurements of ultrafast polarisation change, the reference frequency is halved
to match the chopped pump pulses, such that only changes to the polarisation state due to the pump pulse are recorded. The maximum repetition rate is limited to 20 kHz by the chopper, and to achieve this the beam must be focused through smaller slits in the chopper wheel by a 15 cm achromatic lens and then collimated with an equivalent lens afterwards. For time-resolved measurements, there are multiple options for the probe. White-light generated by a CaF$_2$ plate has the widest range but is noisy and too easily damaged to be used at 20 kHz. Sapphire-generated white-light is more stable and can generate intense white-light at 20 kHz. Also, if the repetition rate is reduced to 1 kHz and the light directed into the CCD cameras after the sample instead, broadband transient absorption and magneto-optic measurements can be carried out without having to change the alignment before the sample. Finally, the other source of light used with the PDs is using the NOPA itself to generate a probe. This setup is shown in Fig.2.6 where a 90/10 beam splitter is used to remove a portion of the pump that can then be frequency doubled and attenuated to be used as a probe. This is very stable and intense, but limits the probe wavelength to half that of the pump. It also means that the probe position at the sample is slightly different to the supercontinuum probe so the overlap must be re-optimised.

2.4 LabVIEW Programs

2.4.1 Broadband CCDs

As previously mentioned, all experiments with the above setup are controlled using a home-built LabVIEW program, since most laboratory equipment came with existing LabVIEW drivers. Therefore once connected to a computer, through ethernet or USB, most functions of the apparatus can be controlled directly by LabVIEW. For measurements making use of the CCD cameras, the program ”StaticandTRMCDandTA.vi” is used. The user interface of this program for static measurements is shown in Fig.2.7. On the left-hand side is a thin beige panel which has many controls common to both time-resolved and static measurements and the rest of the panel is a purple panel which changes depending on the required measurements, through tab selector 1.
Figure 2.7: LabVIEW program used for controlling static MCD and MORD measurements.

The three buttons by 2 in Fig. 2.7 are used for initial alignment of the setup. "Open WL-Spectrum" shows the live spectrum measured by the probe and reference cameras and also their standard deviations. Using this program, the spectrum of the white-light is optimised to get as a broad, intense and stable spectrum as possible. The program is also used to ensure that the wavelengths on the probe spectrum correspond to the same wavelengths on the reference camera, by using the BG36 filter to ensure that all the peaks overlap. Once aligned, the wavelength corresponding to each pixel is calibrated using "Open Calibration". This opens a second program which asks the user to record the transmittance of the BG36 filter. Since the filter has a very well-characterised spectrum, the user inputs the wavelength corresponding to each peak in the measured spectrum through comparison to a calibrated spectrum. A third-order polynomial is fit to the peaks to determine the wavelength corresponding to each pixel on the camera through interpolation. "Get Wavelength Array" imports an existing wavelength calibration.

Section 3 in Fig. 2.7 is used for control of the magnetic field. Custom drivers were written such that LabVIEW can safely control the current and voltage outputted by the PSU. The VISA address of the power supply to the electromagnet is defined as "PSU VISA Address" and "Reset PSU" resets this connection to the PSU. Field direction can
either be controlled manually with a physical switch or through an Arduino connected to a relay switch. The physical switch can handle higher currents of up to 5A (the maximum current that can flow through the magnet without overheating) but has to be switched by hand. In contrast, the Arduino is controlled through LabVIEW to allow for automatic reversal of the magnetic field, although only 4A can flow through the relay switch. Using LabVIEW to turn off the PSU output, reverse the field direction and turn the output back on greatly speeds up measurement time, especially those of static MCD and MORD. The initial direction of the field is controlled with "Initial Field Direction" and the current through the PSU by "PSU Current (A)".

There are several parameters at 4 which affect the process of data acquisition. The "Number of Shots" sets the number of laser pulses over which each data-point should be averaged - typically 1,000-2,000 shots for time-resolved measurements and 3,000-10,000 for static measurements. Anomalous data points are often recorded which have no physical relevance to the signal. These arise from a range of sources such as electrical noise, damage to a particular part of the CaF$_2$ plate or even dust travelling in front of the beam. To remove these points, the top and bottom $p\%$ of points are discarded, where $p$ is set by the user at "Filter Level (%)", and the mean of the remaining data-points recorded. [74] This greatly reduces the noise in a computationally efficient way and, provided $p$ is low (typically 2-5%), then a minimal amount of valid data points are discarded. Finally, "Number of Repeats" sets the number of times the measurement will be repeated. Once a measurement is started, the indicators at 5 give details on how far the measurement has progressed and an estimate of how much real time the remaining acquisition will take.

For static measurements of MCD, there are two main modes of operations indicated by the switch at 6. "Saturation" applies the magnetic field while data is acquired such that the MCD signal measured corresponds to saturation magnetisation in the system, provided the system is saturated below 0.4mT. In contrast, "Remanence" applies the field for a second before it is turned off and then acquisition begins half a second after this. For ferromagnetic systems, the magnetisation aligns with the field and then reverts to the remanent magnetisation once the field is removed, meaning that this
mode allows us to measure the MCD signal due to remanence. An MCD measurement begins with "Start MCD" at 7. The spectrum of the white light for both field directions is plotted in 8 and the MCD, calculated through Eq.(2.4), plotted in 9. Pressing ”Save MCD” in 7 saves the average MCD spectrum and all individual repeats, so that any anomalous spectra can be removed in postprocessing. Additionally, the ratio of the current probe and reference spectra can be recorded and saved using the button in 10.

Time-resolved measurements are more involved than static ones, so a second page in the program is devoted to them, shown in Fig.2.8. Before starting any time-resolved measurement, the spatial overlap of the pump and probe beams on the sample is checked approximately by eye or by using the CMOS camera used for checking the profile of the beams. After this, the program shown in Fig.2.9 is opened using the ”Find Time-Zero” button in Fig.2.8 and used to properly optimise the overlap. The majority of the available inputs and outputs are used for controlling the translation stage which itself controls the delay of the pump pulse. The stage can be moved either to a particular time-delay or forwards and backwards in user-defined steps. After every movement, the current position of the stage and corresponding time-delay are shown in the adjacent indicators. The ”Number of Shots” and ”Filter Level” inputs have the same function as in the main program, except that here they control the acquisition
of the transient spectrum plotted on the right-hand graph. The transient spectrum shows the absorbance change between adjacent pulses (i.e. one with a pump pulse and one without) averaged over the desired number of pulses. Before time-zero or for pump and probe pulses which do not overlap spatially, the spectrum will ideally be 0 mOD everywhere. However, noise in the spectra (arising from WLG or low intensity light reaching the detectors) means that the signal instead flickers around 0 mOD. Furthermore, scattered pump light reaching the detector will cause a large negative signal that is present at all time-delays. This is removed by filtering out as much pump scatter as possible before the detectors or by recording the transient signal at very negative time-delays. At such time-delays, the only change in the spectrum between blocked and unblocked pump will be the scatter so the resulting spectrum of the scatter can be removed from subsequent data in postprocessing. Once a signal corresponding to sample response is obtained, the spatial overlap of the pump and probe beams is optimised by adjusting the mirror directing the pump-beam onto the sample. Next, the time-delay corresponding to the onset of signal at the centre of the range of the white-light spectrum is found and set as the next time-zero. The transient spectrum shown in Fig.2.9 is typical for a spectrum around time-zero. There is a sharp onset in signal around 670nm with several peaks on either side that arise from cross-phase
modulation.

The transient signal recorded by the setup depends greatly on the timing of the CCD cameras and laser pulses. When reading data from the CCD cameras, the computer uses the trigger signal from the laser which has been sent through a delay generator to lengthen and amplify the TTL pulse for detection by the computer. The cameras themselves consist of a 512x128 array of pixels, but these are binned along each column to export a 512x1 array to the computer. This binning makes the detectors much more sensitive and also less prone to slight vertical misalignment of the beam but also slower, with the process taking several microseconds. Therefore the fastest repetition rate the cameras can detect is 1kHz, and this detection is synchronised to the laser pulses using the 1kHz trigger signal. Since this rate is at the upper limit of the detector, the cameras may skip a pulse if the trigger pulse arrives while it is already recording a laser pulse. This makes no difference for measuring the spectrum in real time, but time-resolved measurements rely on the difference between laser pulses where the pulse is on or off. To ensure that spectra of pulses recorded consecutively correspond to ”pump on” and then ”pump off”, the trigger signal of the chopper is also used. This 500Hz trigger signal is non-zero when the chopper blade has blocked the pump pulse and 0 when it may pass. Using this trigger signal ensures that the time-resolved spectrum is always of the same sign over the course of the measurement.

Once the overlap of the pump and probe beams has been optimised, the measurement can begin. A vector of time-delays at which to measure spectra is either created by the program or imported from a text file. The user can then press either ”Start TA” or ”Start TRMCD” to measure a TA or TRMCD spectrum, respectively. The only difference between the two is that a TRMCD measurement has twice as many repeats as a TA measurement, as each repeat must be carried out for both field directions. During the measurement, the signal at a particular wavelength, selected with ”Wavelength /nm” is plotted against time-delay and this can be changed mid acquisition. The top two graphs plot the difference and average of the absorbances for the two field directions after every repeat. The lower graph, ”Full Data”, plots every data-point recorded with linear spacing. Pump-induced heating or damage of the sample or
spontaneous misalignment of an optic can cause a slow change in the signal over time. Since this graph plots all repeats adjacently, long-term changes in the signal between repeats become clear as the measurement progresses. Since the TRMCD relies on the difference between consecutive spectra, such changes in real time can cause erroneous results. To avoid this, if a TRMCD signal is observed, the measurement is repeated except that the opposite field direction is applied first instead. This ensures that the signal observed is field dependent, and not due to real-time changes in the sample.

2.4.2 Bridged Photodiodes

The output of the bridged photodiodes is measured using a lock-in amplifier with the laser repetition rate as its reference frequency. The lock-in amplifier outputs the in- and out-of-phase components of the input, $X$ and $Y$, respectively, and the phase of the lock-in is set such that $Y = 0$ V. The $X$ value is proportional to the rotation or ellipticity change of the sample and is converted through Eq.(2.21) into millidegrees. To measure hysteresis loops, the polarisation change is recorded as the field is swept from positive to negative. However, care has to be taken to ensure that the field is accurate, since there is not a linear relationship between current and field for the electromagnet. The dependence of the field on current starts saturating around 4 A and there is a
Static Spectra

small remnant magnetisation of about 2 mT. To mitigate this, a current of 5A (or 4A for the Arduino-controlled switch) can be applied after the maximum field in each sweep. This ensures that the remanence of the magnet can be accounted for and also that the sample itself is saturated. With this, hysteresis loops at different field ranges are more comparable.

To measure ultrafast polarisation change, the reference frequency of the lock-in amplifier is halved such that the outputted signal is only sensitive to the changes at the same frequency as the pump pulses. This ensures that the signal is proportional to the difference between consecutive probe pulses, as with the CCD measurements. However, this also means that the signal is affected by scattered pump light. To reduce this, filters are placed over both photodiodes to block the pump wavelength but transmit the probe wavelength. To convert the signal into usable units with Eq.(2.21), the single photodiode value, $V_0$, is needed. The output of the lock-in amplifier depends on the power of the probe, as well as the pulse energy, so a change in repetition rate changes $V_0$. Therefore the repetition rate of the laser is halved and $V_0$ measured at this frequency for transient measurements so that both $V_0$ and $\Delta V$ are measured at the same reference frequencies. Pump-probe overlap is optimised in the same way as the CCD measurements, except that the pump-induced signal from the lock-in amplifier is maximised rather than the transient absorbance spectrum. The program used to collect a polarisation trace is shown in Fig.2.10, where the controls on the left are almost the same as in Fig.2.8. With lock-in amplifiers, the time required to acquire a data point depends not on the number of pulses to average over, but rather on the time-constant (and filter order) of the instrument. To ensure that the signal has had chance to settle to the true value, the program waits for ten time-constants before measuring the signal. An infinite settling time is required for the signal to reach the true value and the parameters typically used — a 0.3 s time-constant and fifth order filter — give $\sim 98\%$ accuracy after 3s. Once an acceptable waiting time and set of time-delays have been chosen, a time-resolved measurement can begin. The magnetic field is applied at a constant strength and direction throughout the measurement, and ideally the measurement is repeated with the field in the opposite direction for comparison.
2.5 Testing of the Setup

2.5.1 Static Spectra

To test the accuracy of the setup for static rotation spectra, the Verdet constant, \( V \), of a 1 mm thick piece of soda-lime glass (Thermo Scientific BS7011) was measured, as this is well-studied over a range of wavelengths. The Verdet constant is defined in Eq.(1.6), where it describes the proportionality between the magnetic field strength and Faraday rotation. Faraday rotation, or MORD, spectra of the sample were measured for a range of applied field strengths and a linear fit applied to the data at each wavelength to determine \( V \). Inset to Fig.2.11(a) is one such linear fit at 450nm, where the rotation is clearly well described by a linear dependence on magnetic field. The resulting Verdet constant spectrum is shown by the blue line in Fig. 2.11 (a) and the 68% confidence intervals of the fit are shown by the shaded area above and below the line. Literature values [91] are shown at several wavelengths marked by the red asterisks, and all lie within, or very close to, the error on the measured values.

Both the MCD and absorbance spectra of CoCl\(_2\)-6H\(_2\)O change depending on whether the compound is dissolved in water or concentrated HCl. Because of this it is very commonly used as an indicator for moisture and as such is well studied. [92, 93] Solutions of the compound at a concentration of 0.125 M were made up with distilled water and \( \sim \)37% HCl, and then decanted into a cuvette with a path length of 1 cm. MCD and absorbance spectra were measured for each solution and also for the solvent and cu-
Figure 2.12: Static MCD spectra of a (a) Ni thin film and (c) CoPt bilayer with and without an external applied magnetic field. (b,d) Hysteresis loops for the same samples measured at 450 nm using a laser diode and bridged photodiodes. Both samples are ferromagnetic, but only the CoPt has a remanent magnetisation normal to the sample plane, which is reflected in the square hysteresis loop and the similarities between MCD spectra with the field on and off. The intensity of the supercontinuum below 400 nm is very weak and is unstable above 650 nm, which reduces the signal-to-noise in these spectral regions.

vette themselves. The cuvette especially was found to cause a non-negligible change to the MCD spectra so the solvent and cuvette spectra were subtracted from those of the solution to remove alternative effects. The resulting spectra are plotted in Fig.2.11 (b) and (c) for the aqueous and acidic solutions, respectively, with solid blue lines for the MCD spectra and dotted red lines for the absorbance. Due to the large absorbance of the aqueous solution above 550nm, very little light is transmitted so the MCD in this range is unusable. All four spectra match well with those reported in the literature, with clear peaks at 445, 500 and 525 nm in the acidic and 508 nm in the aqueous MCD spectra, which all lie within <5 nm of the literature values.[92, 93] There is little consensus in the literature as to the absolute magnitude of the MCD spectra themselves, but the spectra shown here are of the same order of magnitude.

Most ultrafast magneto-optics concerns ferromagnetic materials, so MCD spectra were also measured for two ferromagnetic samples: a Ni film and a CoPt bilayer. The Ni film has in-plane anisotropy and was grown through electron-beam physical vapor deposition by H. Lewis on soda-lime glass and is estimated to be around 20 nm thick from
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the growth parameters. The CoPt bilayer was grown on glass by Dr. T. Moorsom from the University of Leeds with the form Ta(4 nm)/Pt(3.5 nm)/Co(1.04 nm)/Ta(5 nm), where the Ta capping layers protect the film. Strong spin-orbit coupling of the Pt layer causes out-of-plane anisotropy in the ferromagnetic Co layer. The saturation and remanent MCD spectra for the Ni and CoPt samples are plotted in Fig.2.12(a) and (c), respectively. Since both spectra are grown on glass, there is a contribution from the substrate to the spectra which could not be removed. Despite this, both spectra show an increase in the MCD signal towards longer wavelengths, and have very different dependencies on the field. Faraday rotation and ellipticity depend only on the magnetic field parallel to the path of the light and so only the out-of-plane magnetisation component is detected in the measurement. This difference in anisotropy is illustrated by the hysteresis loops shown in Fig.2.12(b) and (d), which were measured using a 450 nm diode laser. The contribution of the substrate to the plots is a linear background on top of the ferromagnetic signal of the sample. The effect of the substrate can therefore be removed by determining the gradient of a linear portion of the graph and substracting a straight line with that gradient from the whole plot. Because of this, the substrate contribution has been removed from Fig.2.12(b) and (d) but cannot be removed from (a) and (c), causing a discrepancy between the saturation values of the hysteresis loops and the values of the MCD at 450 nm. There is no measurable hysteresis present in the nickel film, whereas the CoPt shows a very square hysteresis loop. The Ni film has a much higher saturation field than the CoPt but both saturation fields are well below the 400mT field applied in the course of the measurement. This saturation field is lower than would typically be expected in a Ni film of this size which may be due to the formation of a NiO layer on the film, which would be exaggerated by the roughness of the film and substrate. [94] The difference in hysteresis between the two samples is clear in their MCD spectra. Since the nickel film has no out-of-plane remanence, when the field is turned off there is no magnetisation which can affect the transmitted polarisation. In contrast, the remanent magnetisation of the CoPt bilayer is almost the same as its saturation magnetisation, so one would expect to see minimal change in the MCD spectrum once the field is removed. This is exactly what is observed, showing the
Figure 2.13: Demagnetisation of a Ni film exposed to an 800 nm, 5 mJ cm$^{-2}$ pump pulse. (a) Time-resolved MCD and (b) Transient transmittance spectra, where the signal below 400 nm is reduced due to the small intensity of the supercontinuum at shorter wavelengths. The pump scatter can also be seen at wavelengths other than 800 nm and is characterised by a signal at negative time delays. (c) Transient ellipticity and rotation at 550 nm, averaged over 5 nm. (d) Magnetisation change at $t = 1.5$ ps after the pump pulse, calculated from both ellipticity and rotation. Dividing by the much noisier static spectra increases the noise level but both show roughly the same demagnetisation across the spectrum.

sensitivity of the setup to magnetisation direction. Both samples have relatively low transmittance but the CoPt transmits less, and this results in a higher level of noise in the CoPt data in Fig. 2.12 (c). The CoPt spectrum with field on is clearly noisier, but the reasons for this are unclear. No field dependence is observed in the noise so it is likely due to a more noisy supercontinuum for that particular measurement.

### 2.5.2 Time-Resolved Spectra

Testing of the time-resolved measurements was carried out on the aforementioned Ni film. Pump pulses with wavelength 800 nm, duration 120 fs and fluence 5 mJcm$^{-2}$ were used. The high fluence produced a lot of scattered pump light, and so a polariser was used to remove this contribution. The sample was held at room-temperature and an external magnetic field of 0.4T was applied. The TRMCD, TRMORD and TA were calculated from the raw data using Eqs. ((2.13)) and ((2.14)), respectively, and then corrected for the impact of the polariser with Eq.(2.17). The resulting contour plots are shown in Fig. 2.13 (a) and (b). The TA has been multiplied by $-100\ln10$ to convert
into percentage change in transmittance since the film has non-negligible reflectance. There is a clear change in the sample following the pump pulse, with non-zero values for both the transmittance and TRMCD persisting well beyond the duration of the pump pulse. The TRMCD shows slight wavelength dependence and a rapid demagnetisation with a rise time of 0.3 ps. This decays with an exponential decay of 2 ps, after which the spectrum stabilises to a plateau. Such dynamics can be explained phenomenologically with the three-temperature model.[31] The transmittance change has a similar initial rise time of 0.3 ps, but after this has clear spectral dependence. Redder wavelengths show a larger and longer lasting change in transmittance. At 650 nm there is signal at negative times that shows no time dependence, which is indicative of scattered pump light. This pre-time-zero signal approximates the pump scatter across all time-delays and so can be subtracted from the remaining data to remove the effect of pump scatter.

To obtain the ellipticity and rotation changes plotted in Fig.2.13(c), a 5 nm Gaussian weighted average was applied to the spectra at 550 nm. These traces more clearly show the polarisation change over the first couple ps.

Dividing the TRMCD and TRMORD by their static counterparts gives the percentage magnetisation change. The MCD and MORD spectra of a glass slide, like the one on which the Ni film was grown, were measured under the same conditions as for the saturation spectra in Fig.2.12(a). These could then be subtracted from the static MCD and MORD spectra of the nickel sample, recovering the spectrum of the nickel itself. From these and their transient counterparts, the percentage magnetisation was calculated. A peak demagnetisation of ca. 16% is observed, which is of the expected order of magnitude for such films and fluences. [32, 95] Plotted in Fig.2.12(d) is the spectral dependence of the demagnetisation at 1.5 ps, calculated from both the MCD and MORD spectra. The signal-to-noise is significantly lower than in Fig.2.12(a-c) because the static spectra, especially when subtracted from one another, have inherently higher levels of noise. The noise in the static spectra accounts for the decrease in magnitude below 450 nm and the oscillations above 600 nm. However, no other spectral dependence is observed and the demagnetisations calculated from the TRMCD and TRMORD are roughly the same. The magnetisation change should be independent of
Comparison of Photodiode and CCD Schemes

The measurements shown in Fig.2.13 use white light generated in CaF$_2$ using 800 nm pulses at 1 kHz using the Legend laser. By flipping down a mirror and inserting a bandpass filter, a trace at a single wavelength can be measured using the photodiodes. The percentage change in magnetisation can then be calculated using the polarisation change corresponding to a saturation magnetisation in the hysteresis loop. A 543 nm bandpass filter was used to measure the ellipticity trace shown in Fig.2.14 for the PDs and a gaussian weighted average used to get the trace from the CCDs. The difference in noise between the two is clear. Converting the TRMCD to magnetisation only introduces noise between wavelengths, not between time-delays. The noise level of the CCD array is roughly 1 mdeg for single pixels but the weighted average reduces this to 0.4 mdeg. As can be seen in Fig.2.14, this is about an order of magnitude smaller than wavelength and method of measurement so this further confirms that we are indeed measuring both static and transient changes in ellipticity and rotation.

2.5.3 Comparison of Photodiode and CCD Schemes

Figure 2.14: Demagnetisation of a thin Nickel film at 543 nm probe using 800 nm pump measured with both the CCDs and PDs, using the same fluence for each. For both cases, the probe is at 1 kHz and generated from a CaF$_2$ supercontinuum. While both traces overlap well, the CCDs clearly have greater signal-to-noise.
Figure 2.15: Comparison of transient rotation change of a thin Ni film pump with 800 pump pulses of the same fluence, using the CaF$_2$ supercontinuum as a probe with the CCD cameras and the NOPA as a probe with bridged photodiodes.

The sensitivity of the bridged PDs when measuring the same demagnetisation. Of course averaging over more repeats will reduce this noise further, but both measurements had similar acquisition times. The CCD arrays are also more sensitive at low light levels than the bridged photodiodes and the reference beam means one can account for shot-to-shot and spectral fluctuations.

Instead of increasing the acquisition time to average over more pulses, one can also increase the repetition rate. This was not possible with the Legend but repetition rates of up to 25 kHz are possible with the Pharos. A major limitation of the CCDs is that they only work at 1kHz, whereas the bridged photodiodes can acquire data at significantly higher repetition rates. Therefore, with the variable repetition rate of the 1028 nm Pharos laser, the sensitivity of the bridged PDs increases greatly. Instead of the detector, the maximum repetition rate is now limited by the chopper, through which light must be focused in order to reach a pumping rate of 10 kHz. However, this focusing requires lenses which can increase the pulse length and the change in repetition rate changes the shape of the beam slightly. Therefore, to check that measurements at higher repetition rates are still comparable to 1kHz broadband measurements, the demagnetisation of the nickel film was measured using a 12.5 kHz repetition rate. The sample was pumped at 800 nm and probed with 400 nm light generated using CaF$_2$. 


Comparison of Photodiode and CCD Schemes

Figure 2.16: Stability of the sapphire white light over time.

for the broadband measurements and by doubling the 800 nm output from the NOPA for the photodiodes. A 10 nm wide gaussian weighted average was applied to the transient spectrum from the CCD measurement to obtain the trace for the CCDs. These two traces are plotted in Fig.2.15, where they clearly match very well, showing the equivalency of the higher repetition rate and the two detection schemes. The peak before time-zero in the PDs trace is due to a non-linear artefact to which the PDs are more sensitive. Contrary to Fig.2.14, the noise is slightly better in the PD data rather than the CCDs - roughly halving between the two. A major reason for this is the sources of probe light, as the NOPA is inherently more stable and much more intense than the CaF$_2$. The higher repetition rate allows for a much higher rate of repeats, which also improves the sensitivity.

The frequency-doubled NOPA is clearly an effective probe but it limits the available probe wavelength to half the pump wavelength. Also, using a different source of probe pulses to the broadband measurements makes it time-consuming to switch between measurement schemes when needed. While CaF$_2$ is too easily damaged, supercontinua can be generated in sapphire at repetition rates well above 20 kHz. However, the sapphire plate used for white-light generation is held stationary, so heating and slow degredation of the medium over time is potentially a concern. To test this, the single photodiode voltage of the sapphire supercontinuum at 543 nm at 20 kHz was measured.
over time. A half-wave plate was used to balance the PDs before blocking one and recording the drift of the signal over the next two hours. The results are plotted in Fig.2.16, where the signal changes by about 1% over the course of the measurement. The signal increases over time, either due to an increase in intensity or a change in polarisation. A long-term change in the polarisation of the probe will have negligible effect on the measurement, as long as it is small enough that Eq.(2.21) still holds. If the intensity changes by 1% over the course of a measurement then the measured signal will also change by about 1%. Since this is typically comparable to or smaller than the noise, such drift is negligible.

Using higher repetition rates means that a higher average power is incident on the detector. It is important that the signal from the photodiodes scales linearly with the power incident on them, since otherwise this non-linearity may skew experimental results. This was measured using the 400 nm light generated from the 800 nm NOPA output as this is the most intense probe source used. There was no sample used in place of the beam, but instead several interchangeable neutral density filters were used to attenuate the beam a known amount. One photodiode was blocked and the single photodiode voltage recorded for various intensities. The power of the beam is too small

Figure 2.17: Scaling of the photodiode signals with intensity. (A) Single photodiode voltage at 20 kHz against transmittance. (B) Transient rotation signal of the Ni film pumped with 800 nm, arbitrary fluence pump pulses at 1 ps against single photodiode voltage. A linear fit which passes through (0,0) shows the linearity of the data.
to be measured outright with a power meter, so the optical density is estimated from the nominal absorbances of the filters. This voltage is plotted against the estimated transmittance in Fig.2.17(A). The plot appears to have two regions where $V_0$ is linear with transmittance and has a turning point around 13 mV. To investigate the effect of this on transient measurements, the ND filters were replaced with the nickel film. To ensure that the temporal overlap between the pump and probe beams remained constant while changing the probe intensity, a graduated neutral density filter was placed in the path of the probe instead of several individual ND filters. Initially, a field was applied, the pump blocked and the photodiodes balanced, after which the single photodiode voltage was recorded. An 800 nm pump of arbitrary fluence was used to pump the sample and the difference signal at 10 kHz was recorded at a 1 ps time-delay. The 10 kHz signal is plotted against the single photodiode voltage in Fig.2.17(B), and a linear fit to the data is also shown. Since the pump fluence and time-delay are constant, the ratio between the transient signal and $V_0$ should be constant. The data are almost exactly linear so this relation holds, and the response of the photodiodes for transient signals is intensity independent over the range investigated. Such a range is typical of those used in these experiments. This linearity observed in the time-resolved signal but not the single PD voltage is likely due to the size of the signal itself. The output of the difference channel of the PDs is optimised for small signals so the outputted voltage is likely more accurate for small signals and saturates somewhat at large voltages.

2.6 Other Experimental Methods

2.6.1 Atomic Force Microscopy

Atomic force microscopy can measure the dimensions of nanostructures with almost atomic precision. [96] The microscope consists of a cantilever with a sharp tip that oscillates at its resonant frequency. Modes of operation where the tip makes contact with the surface are also possible but risk damaging the surface or tip. Piezoelectric elements precisely control the position of the tip and bring it close to the surface to be measured. Intermolecular forces between the tip and the surface, such as van der Waals
forces, change the resonant frequency of the tip and this frequency therefore depends on
the distance between tip and surface. As the tip is moved across the surface laterally,
its height is adjusted to maintain a constant resonant frequency. This results in a map
of the height of the sample, without making contact with it. The frequency of the
tip itself is often measured by reflecting a diode laser off of the back of the tip and
measuring its deflection. Through this process, the height profile of small samples can
be measured, as well as their surface roughness.
Chapter 3

Ultrafast Demagnetisation and Photoexcited Electron Dynamics in the van der Waals Ferromagnet Cr₂Ge₂Te₆

The work presented in this report is adapted from a submitted manuscript.

Layered materials consisting of (few-)atom thick sheets held together only by van der Waals forces show promising intrinsic properties for use in future technologies, from high mobility in graphene [97] to room temperature excitons in transition metal dichalcogenides. [98, 99] A single isolated layer of these materials is effectively two-dimensional, thus van der Waals crystals are often called 2D materials. These materials may show a strong dependence on their properties with the number of layers, such as a change from indirect to direct band gap in semiconductors [100] or a change from para- to ferromagnetic ordering. [101] Furthermore, individual layers can be stacked together to form heterostructures with atomically fine boundaries [102], an essential quality for effective device fabrication. Countless such heterostructure devices have been formed, from p-n junctions for use in photovoltaics [103], to tunnel junctions [104] and to excitonic lasers [105].

Magnetic materials are of great technological importance, most notably in mag-
netic memory but also in emerging spintronics, so 2D magnetic materials have been of interest for decades. However, besides reports of ferromagnetism along boundaries or edges of graphene nanostructures [106], no such material was discovered until 2017. The simultaneous discovery of the first two 2D ferromagnets, CrI$_3$ [107] and Cr$_2$Ge$_2$Te$_6$ [108], sparked much interest in the potential of van der Waals crystals in magnetic devices and many other 2D magnetic materials have since been discovered. [109–111] In its bulk and monolayer forms, CrI$_3$ is ferromagnetic, so the inter- and intralayer coupling was expected to be ferromagnetic. However, bi-layer CrI$_3$ is antiferromagnetic, and this antiferromagnetic interlayer coupling persists for hundreds of layers, becoming ferromagnetic in the bulk. This interlayer coupling opens up a new parameter with which to manipulate and understand magnetism in materials.

Like many phase transitions, magnetism depends strongly on dimensionality. Long-range magnetic order is driven mainly by the balance between the exchange interaction and thermal fluctuations. The Curie temperature, $T_C$, is the temperature below which the short-range exchange interaction can overcome the randomising effect of thermal energy. Magnetic phase transitions can always occur at finite temperatures in 3D systems, yet are only possible at absolute zero for 1D systems, and 2D systems lie between the two. [109] From the Mermin-Wagner-Hohenberg theorem [112, 113], 2D systems obeying the isotropic Heisenberg model — where spins can point in any direction — cannot magnetically order above $T = 0$ K. This is because the continuous symmetry of the isotropic system enables the generation of low energy magnons (quantised spin-waves) by arbitrarily small thermal fluctuations, which in turn prevents magnetic phase transitions at $T > 0$ K. However, in the presence of uniaxial magnetic anisotropy (an easy axis), these low-energy magnons are suppressed and so long range magnetic ordering is possible at a finite temperature. [108] Easy plane anisotropy leads to a complex topological phase transition rather than an in-plane magnetisation. [109] Because of this, most 2D ferromagnetic materials have out-of-plane magnetisation in the 2D limit, which makes them ideal for many technological applications. Furthermore, Faraday rotation and ellipticity are only sensitive to the component of magnetisation along the direction of propagation so this anisotropy is convenient for magneto-optical
measurements. This dimensionality dependence is typically fairly weak and is only present at the monolayer or few-layer limit however. [109]

Both CGT and CrI₃, as well as the many of other 2D magnetically-ordered materials discovered thus far, are semiconductors. A consequence of this is that, at the low temperatures required for magnetic ordering, conductivity is often very low. [114] Thin, exfoliated crystals are typically very small and therefore are unsuitable for SQUID magnetometry. Therefore, characterisation of their magnetic properties is typically measured optically with Kerr microscopy. As the name suggests, this uses a tightly focused continuous-wave laser beam to measure the Kerr rotation of a small area. Not only does this allow for position dependent measurements, but freshly exfoliated samples are typically very clean so reflect light well with minimal scatter. Transport measurements can also be used to indirectly measure magnetism by creating a non-magnet/ferromagnet heterostructure and measuring the induced anomalous Hall effect in the non-magnet — typically graphene — layer. [115, 116] Furthermore, the most technologically useful property of semiconductors is that a gate voltage can be applied across the material to control carrier concentration. This of course applies to magnetic semiconductors as well, and the effect can be even stronger in 2D materials, with their intrinsically high surface-area-to-volume ratios. Gate-induced doping can drastically affect magnetic properties, increasing coercivities [117] and Curie temperatures [118] and also affecting magnetic anisotropy. Functionalisation of these materials through adsorption [119] or intercalation [120] can also have a drastic effect on magnetic properties, providing another means through which to tune material properties.

CGT is a van der Waals semiconductor which is ferromagnetic at low temperature [121]. It is a soft ferromagnet with weak remanence and out-of-plane anisotropy, whose $T_C$ varies throughout the literature from about 60–70K for the bulk sample depending on measurement technique or crystal growth. [108, 114, 122–125] As the number of layers is reduced, $T_C$ reduces greatly [109] and the anisotropy remains uniaxial for all but the monolayer case. [126] Application of a small magnetic field along the easy axis can increase the bilayer $T_C$ from 4.7 K to 41 K, likely because the external uniaxial magnetic anisotropy suppresses low-energy magnons.
The band gap of CGT is indirect and about $\sim 0.7$ eV wide [126] so the absorption edge is rather shallow and lies within the mid-IR. High temperature absorption spectra in the visible region are shown in Fig. 3.1 where the absorbance increases monotonically to a peak around 380 nm. No high-resolution spectra could be found at low temperature, but all spectra at room temperature [127–129] show no features besides a shallow increase towards the blue. Calculated spectra show some features but are less reliable. [116, 126]

Within CGT, each Cr$^{3+}$ ion is approximately octahedrally coordinated to six Te$^{2-}$ ions and Ge$^{3+}$ dimers are spaced throughout. This can be seen in the crystal structure of CGT shown in Fig. 3.2. Because of the $90^\circ$ Cr–Te–Cr bond angle,[121] the Cr $e_g$ and Te $5p$ orbitals overlap and can hybridise. The Cr$^{3+}$ ions are $d^3$ and, excluding any hybridisation, the ligand field splitting results in an occupation of $t_{2g}^0e_g^0$, where all three $t_{2g}$ electrons have the same spin. A schematic of the spin-projected density of states (PDOS) is shown in Fig. 3.3 A. Previous calculations of the PDOS in CGT indicate that the Te and Ge orbitals are mostly delocalised whereas the Cr orbitals are more localised [126, 130, 131]. The band gap in the material is formed by the Te $5p$ valence band edge and the $(5p - e_g)^*$ conduction band [130] [132].
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Figure 3.2: Crystal structure of CGT with (a) side and (b) top-down views. The $c$-axis points perpendicular to the atomic layers.

Figure 3.3: (a) Schematic of the projected density of states of CGT. (b) Nominal ionic electronic configuration, where non represents an additional non-bonding $5p$ state. (c) Electronic configuration taking hybridisation into account. $J^\text{Cr}_{H}$ and $J^\text{Te}_{H}$ represent the exchange coupling within the Cr and Te ions, respectively. (b,c) are reproduced from Watson et al. [121]
Ferromagnetic ordering arises in the material through superexchange due the $(5p-e_g)$ hybridisation. A schematic of this process is reproduced from Ref.[121] in Fig.3.3 B,C, showing the electron occupancies in the limiting cases of no and full hybridisation. Hund’s rule coupling between $t_{2g}$ and $e_g$ electrons, represented by $J_{H}^{Cr}$, makes it energetically favourable for all $d$ electrons on the Cr ion to have the same spin. At the same time, Hund’s rules also make it favourable for both the unpaired $5p$ electrons to have parallel spins, with the coupling between them represented by $J_{H}^{Te}$. The hybrid $(5p-e_g)$ orbital is therefore occupied by a single electron whose spin must match the spin of the $t_{2g}$ electrons and also be antiparallel to the spin in the corresponding $5p$ orbital. Hund’s rule coupling within the $5p$ orbitals therefore causes the $t_{2g}$ electrons on the Cr ions either side of the bond to lie parallel. This results in more majority spin Cr-centred states below the band gap and more minority spin above due to the energy penalty involved with a spin flip. Superexchange is well understood in materials with specific bond symmetries and has been shown in CGT through X-ray MCD (XMCD) measurements which observed the change in magnetic moment on the different ions. A model assuming a Cr $d$-electron count of 3.5 reproduced experimental results, suggesting that the true case is halfway between Fig.3.2 B and C. The magnetocrystalline anisotropy resulting from this superexchange means that the easy-axis lies out-of-plane along the $c$-axis. However, this coupling is relatively weak, leading to the low Curie temperature and a low saturation magnetic field.

Magneto-optical spectra are sensitive to different aspects of electronic structure than absorption spectra. Therefore, despite the relatively featureless absorption spectrum of CGT in the visible, it is predicted to have a rich magneto-optical spectrum. The calculated Faraday rotation and ellipticity for bulk and monolayer CGT are plotted in Fig.3.4 C,D, respectively. Corresponding Kerr spectra were also calculated (Fig.3.4 A,B) and show similar richness of structure, but are less relevant to the studies presented in this work. All four spectra in Fig.3.4 are non-zero but flat at low energy, with an almost oscillatory behaviour at higher energies. The predicted Kerr rotation at 0.8 eV matches well the value measured by Gong et al. in few-layer CGT [108]. At 2.9 eV, the rotation reaches its maximum magnitude of mdeg/µm. Since this is
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Figure 3.4: Calculated (a,b) Kerr and (c,d) Faraday spectra for (a,c) bulk and (b,d) monolayer CGT from Ref.[126]. Rotation is shown in red and ellipticity in blue.

similar to the highest measured Faraday rotations,[133] CGT shows great potential for magneto-optical studies if this value turns out to be true. The rotation and ellipticity have similar shapes but appear to be almost a quarter-wave out of phase with each other. This is likely partly due to their origins in the real and imaginary components of the off-diagonal components of the complex dielectric tensor. [16] This strong spectral dependence shows how broadband techniques are needed to fully optically characterise these materials. Within the spectral range accessible with our setup ($1.6 - 2.6$ eV), the ellipticity is predicted to be larger and show stronger variation than the rotation.

Fang et al. assign features in the complex optical conductivity tensor to transitions within the CGT band structure. However, they do not assign features in the Faraday or Kerr spectra, due to the complex relationship between the optical conductivity and magneto-optics. Furthermore, since charge carriers occupy bands rather than discrete levels, peaks corresponding directly to specific transitions are typically very broad and overlap, making it difficult to assign optical spectra. Finally, the spectra appear quite similar between monolayer and bulk systems, except for a larger response in the IR for bulk.

Since CGT was one of the first discovered 2D materials and it has a much smaller and more accessible coercive field than $\text{CrI}_3$, it is often used as a model system and
has been studied extensively. [134–139] Most relevant to the work reported here are ultrafast studies of CGT. Zhang et al. [52] measured transient Faraday rotation at 815 nm following photoexcitation by 770 nm, 0.123 mJ/cm² pump pulses at 78 MHz. Their sample was a single 3.5–20 nm thick CGT crystal encapsulated between two flakes of hBN and they had a spatial resolution of 2 µm, so could accurately probe only their crystal. A fast initial demagnetisation which recovered over several nanoseconds was observed, but it precessed with frequencies of 5-20 GHz. The sample and field were rotated to determine the dependence of the frequency and damping of the oscillations on angle and field strength, which allowed the authors to determine the anistropy field and the damping of the oscillations. The observed damping was much lower than most ferromagnetic materials with perpendicular magnetic anisotropic, which the authors state is due to a very weak spin-orbit interaction and limited electron-electron scattering events due to more localised electrons.

Oscillations were also observed by Guo et al. [140], but in the transient reflectance when pumped and probed at 800 nm. They observed two oscillations with periods of 240 and 290 fs, which they assigned to the $E_g^3$ and $A_g^1$ Raman active modes respectively, and measured their temperature dependence. While the $A_g^1$ mode only showed slight temperature dependence, the ”larger” $E_g^3$ mode became significantly more intense below $T_c$. The authors therefore state that this mode is due to a spin-coupled phonon mode that can only exist in the presence of long-range magnetic ordering. The transient reflectance was also found to double when an magnetic field was applied, but the paper gives no explanation of this.

Transient transmittance was also measured for the closely related CrSiTe₃ (CST) by Ron et al. [132] Since the Si atoms contribute little to the magnetic behaviour except for acting as spacers, the Si analogue of CGT is expected to have similar properties. [125] The group observed an initial decrease and subsequent recovery of the reflectivity on a ~2 ps timescale, which also showed strong 3.8 THz oscillations that they attribute to the $A_g^3$ mode. The temperature and pump-wavelength dependence of these oscillations suggests that the photoexcitation modulates the pump-probe excitation. Similar dynamics were observed by Suo et al. [141] with THz emission spectroscopy, where
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Figure 3.5: Demagnetisation dynamics of three different ferromagnets at (a) short and (b) long times, reproduced from Ref.[51]. CGT shows a distinctive two-step demagnetisation, whereas CT and FGT show only the first step.

they saw a biexponential decay with $\tau_1 \sim 3 - 4$ ps and $\tau_2 \sim 23$ ps. They assign the former to electron–phonon coupling and the latter to the surface phonon/defect-mediated electron–hole recombination process.

Ultrafast demagnetisation of not only CGT, but also $\text{Fe}_3\text{GeTe}_2$ (FGT) and $\text{Cr}_3\text{Te}_4$ (CT) was investigated by Sun et al. [51] They measured Kerr rotation at 400 nm for freshly exfoliated samples at low temperature, using 800 nm pump. Their results are shown in Fig.3.5, which illustrates the differing magnetisation properties of the materials. CGT clearly shows Type II dynamics, with two demagnetisation steps before reaching its peak demagnetisation after several hundred ps. They also observed a transition from Type II to Type I dynamics as fluence decreased. FGT is a layered ferromagnet like CGT but is metallic rather than semiconducting. This causes a faster initial demagnetisation than CGT, but still takes a relatively long time to full demagnetise and has a very slow recovery. In contrast, CT is a 3D metallic ferromagnet which shows clear type I dynamics due to its strong electron-spin coupling. FGT has a similar conductivity to CT but electrons can only scatter within layers, which greatly limits electron-spin coupling and results in dynamics intermediate between types I and II. This also affects CGT, but it has a much lower conductivity as well, leading to even lower coupling and therefore type II dynamics.

As demonstrated by Sun et al., CGT is not the only 2D magnet whose ultrafast properties have been studied. $\text{CrI}_3$ has also been studied in Kerr geometry, also showing
Type II demagnetisation and spin waves, whose frequency can be manipulated with an applied gate voltage.[142] Pump helicity was found to strongly affect spin-waves in CrI$_3$ and also drive all-optical magnetisation reversal. [143, 144]

All of the above studies use monochromatic probe and none take into account the effect of probe wavelength on the polarisation dynamics. Therefore, I have measured transient ellipticity and transmittance at low temperature with a broadband probe using the method described in chapter 2. Unless otherwise stated, all measurements were carried out at 20 K using linearly polarised, 800 nm and 1.0 mJcm$^{-2}$ (0.5 mW) pulses as a pump.

### 3.1 Sample Characterisation

The sample measured to produce the results shown here was fabricated by S. Xingjian in the Eda group at the National University of Singapore and is referred to as sample A where necessary. Bulk crystals of CGT were first grown through chemical vapor transport in a similar manner to previous work.[123] These crystals were then exfoliated manually to form small, exfoliated flakes of the material. By looking at them under a microscope, thin flakes of uniform thickness were chosen and then deposited on a glass substrate. A monolayer of hexagonal boron nitride was placed over the crystal to protect it before finally a layer of chromium metal was deposited over the substrate. This metallic layer had two 200 $\mu$m holes, one centred on the sample and the other which only left substrate uncovered. With both holes, the signal from the sample plus substrate and just the substrate can be compared. Since the metallic mask is opaque, the holes make alignment onto the crystal significantly easier.

A zoomed-in image of the sample is shown in Fig.3.6, where it can be seen that there are three small crystals in the sample hole. As is typical for van der Waals crystals, the colour of a crystal is linked to its thickness. The upper-right crystal is small so unlikely to contribute to our measurements. By far the largest crystal is 40x20 $\mu$m and there is a smaller, much thinner, $\sim$10x20 $\mu$m crystal next to it. It is therefore expected that the majority of the signal originates from the larger crystal. However, since both are
much smaller than the probe beam, it was impossible to select a particular crystal.

The thickness of the sample was measured by atomic force microscopy (AFM) several weeks after the measurements described subsequently were carried out, so the sample had most likely oxidised somewhat. AFM images of the two crystals are shown in Fig.3.7 along with height profiles at three Y positions. To account for a slight slant in the substrate during the measurement, a linear fit of the far left and right points was subtracted for each Y position. Oscillations are visible around $Y = 15 \, \mu m$ in A and throughout in B which are an artefact of the measurement technique rather than physical ripples. From the height profiles, the thickness of the larger crystal is clearly around $90-100 \, nm$ and the smaller is around $10 \, nm$ thick. While a oxide layer could be present on the sample, the $90$ and $10nm$ thicknesses of the larger and smaller crystals shown in the figure are expected to be similar to the original sample thicknesses. This corresponds to several hundred layers of CGT.

The crystal of CGT is smaller than we are able to focus the beam. This greatly increased the noise of the experiment, as well as making it much more difficult to align accurately, so the measurement of reliable static ellipticity, rotation or transmittance spectra was not possible. For transient measurements, the spatial and temporal overlap was optimised first, then the sample moved to maximise the transient transmittance signal. The signal was very sensitive to sample position so the measurement was repeated if the sample moved (signified by a sudden drop in signal) and position was optimised before every experiment.
Chapter 3.2.0

Since CGT is known to be very air-sensitive,[145] the fabrication was carried out under inert atmosphere and the samples were sent to us in an airtight container. To prevent oxidation, sample A was only opened immediately prior to measurements and was mounted onto and unmounted off of the cryostat in a glovebox under nitrogen atmosphere.

3.2 Transient Ellipticity

The transient ellipticity spectrum with the sample held at 20 K and using a pump power of 1.0 mJcm\(^{-2}\) is plotted in Fig.3.8 A, with traces at selected probe energies plotted in B. This measurement was repeated on just the substrate and no polarisation change above the noise level of the detectors could be observed. From the contour plot, there is clear wavelength dependence to the spectrum and the spectrum is different at short and long times. At short times, there appear to be two quickly-decaying positive peaks around 2.2 and 1.8 eV with negative, slowly-growing peaks between them. At longer times, the positive peak at 2.2 eV has disappeared and the peak at 1.8 eV is only
just visible above the noise but the broad negative peak around 2.0 eV continues to increase in magnitude before plateauing around 300ps. The kinetic traces in Fig.3.8 B show this more explicitly. At 2.0 eV, the ellipticity shows a sharp initial decrease followed by a slow, monotonic decrease before plateauing around 300 ps. At 2.2 eV, the ellipticity increases sharply on the timescale of the pump pulse, after which it decreases monotonically before also plateauing around 300ps. Therefore, around 5ps, no ellipticity change is observed at 2.2 eV, yet a clear negative change is observed at 2.0 eV. A change proportional to magnetisation dynamics is not observed here due to overlapping transient features, so we need some way of disentangling the demagnetisation from the other transient effects.

3.2.1 Global Fitting

Transient absorbance data are typically fit to a sum of several exponential decays with different time constants. These time constants approximately correspond to the rate constants of different steps of the decay process. In reality, and especially so in crystalline systems, decays are most accurately described by continuous distributions of time-constants across both spectral and time domains. However, if the data are noisy and there is little a priori knowledge of the decay process, continuous distributions are practically impossible to fit to data. Furthermore, even decays resulting from Gaussian
distributions of time constants are well-described by a bi-exponential decay. Care must therefore be taken to not over-parameterise or over-interpret when fitting with discrete time-constants.

Multi-exponential fits are often applied to kinetic traces at individual wavelengths. Mathematically, the fit applied to the kinetic trace at a particular wavelength, $D_{fit}(\lambda', t)$, is given by the sum of $n$ exponentials convoluted with the instrument response function (IRF)

$$D_{fit}(\lambda', t) = \sum_{i=1}^{n} A_i e^{-(t-t_0)/\tau_i} \otimes e^{-\frac{(t-t_0)^2}{2\sigma^2}}$$

(3.1)

where $t$ is the time-delay. The IRF here is assumed to be a Gaussian centred on $t = t_0$ and with width (or pulse length) $\sigma$. Each exponential term has an amplitude, $A_i$, and time-constant, $\tau_i$, which act as the fitting parameters. Least-squares or other fitting algorithms can then be used to fit as many exponentials as needed to the data using Eq.(3.1). However, our spectrometer produces a continuous spectrum of up to 512 individual traces (one for each pixel). Fitting several exponentials to each trace would be very inefficient and likely give different time-constants for each trace, making interpreting the fit difficult. Instead, an alternative approach is to assume the same set of time-constants across the whole spectrum and instead encode the spectral dependence in the amplitudes. This results in

$$D_{fit}(\lambda, t) = \sum_{i=1}^{n} A_i(\lambda) e^{-(t-t_0)/\tau_i} \otimes e^{-\frac{(t-t_0)^2}{2\sigma^2}}$$

(3.2)

$$= \sum_{i=1}^{n} \frac{A_i(\lambda)}{2} \exp\left(\frac{t-t_0}{\tau_i} - \frac{\sigma^2}{2\tau_i^2}\right) \left[1 + \text{erf}\left(\frac{t-t_0-\tau_i^{-1}\sigma}{\sqrt{2}\sigma}\right)\right]$$

(3.3)

$$= C(t)^T \cdot S(\lambda)$$

(3.4)

which is similar to Eq.(3.1), except that it now depends also on wavelength. To ease fitting, the convolution is evaluated explicitly in Eq.(3.3) using the error function, erf().

Using matrices to make the sum implicit, Eq.(3.3) is rewritten in a bilinear form in Eq.(3.4). If the measured spectrum, $D_{meas}(\lambda, t)$, is measured at $l$ wavelengths and $m$ time-delays, the 2D spectrum will have dimensions $l \times m$. For $D_{fit}(\lambda, t) = D_{meas}(\lambda, t)$, then $S(\lambda)$ has dimensions $n \times m$ and $C(t)$ has dimensions $n \times l$. Therefore, each row
in $S(\lambda)$ corresponds to a different $A_i(\lambda)$ in Eq.(3.3) and each row in $C(t)$ corresponds to the kinetics described by each $\tau_i$. Importantly, this step makes the assumption that the 2D spectrum is bilinear, such that $\{\tau_i\}$ and $t_0$ do not depend on $\lambda$ and $\{A_i(\lambda)\}$ on $t$. Thus the data must be chirp corrected to remove the spectral dependence of $\tau_0$ before the fit can be applied.

Without an analytical expression of the spectrum, $A_i(\lambda)$ cannot be fit to the data. However, with the data in a bilinear form and assuming that $D_{fit}(\lambda, t) = D_{meas}(\lambda, t)$, $S(\lambda)$ can be calculated instead. Given an initial guess for $C$, the corresponding $S_{fit}$ that recreates $D_{meas}(\lambda, t)$ can be determined through

$$S(\lambda) = D_{meas}(\lambda, t) \cdot C^+ \quad (3.5)$$

where $C^+$ is the Moore-Penrose pseudoinverse of $C$. [46, 147] Since $C$ is not always square, it does not have a true inverse, but the pseudoinverse has similar properties. [148] The fit to the whole TA spectrum, $D_{fit}$ is therefore given by

$$D_{fit} = D \cdot C^+ \cdot C \quad (3.6)$$

The accuracy of the fit is then determined by the absolute difference between the measured and fitted spectra. By using Eq.(3.6) to determine the fit to the data, no $a\ priori$ knowledge of $S(\lambda)$ is required and all the fitting parameters are only used to define $C(t)$. To fit the data, the fitting parameters — $\{\tau_i\}$ in Eq.(3.3) — are varied to minimise $|D_{meas} - D_{fit}|$. Computationally, this is achieved using the MATLAB function `lsqnonlin` which uses a non-linear least squares algorithm to achieve this minimisation by varying $\{\tau_i\}$. The output of the fit is of course $D_{fit}(\lambda, t)$ and the optimised parameters, but also $S(\lambda)$ and therefore $\{A_i(\lambda)\}$. Each $A_i$ gives the component of the spectrum that decays a rate of $\tau_i^{-1}$ so these are termed decay-associated spectra (DAS).

Because Eq.(3.4)-(3.6) make no assumptions about the form of $S(\lambda)$ and $C(t)$, aside from that they depend on either $\lambda$ or $t$, the time dependence of $C(t)$ is not required to be exponential and can take almost any form. Furthermore, Eq.(3.4) can also be rearranged to calculate $C(t)$ from an $S(\lambda)$ of known form in much the same manner.
Globally fitting data to a multi-exponential model is typical in analysis of transient absorption spectra across a range of timescales. [46, 147] The method described above is one commonly used method of fitting,[149] but there are several other methods to achieve this, and many software packages which can make this process easier, the most common of which is Glotaran.[150] Therefore, to test the applicability of my fitting procedure, the transient absorption spectrum of an organometallic ruthenium complex in solution acquired by K. Barlow was analysed. The decay associated spectra from both methods are plotted in Fig.3.9 and, while their physical interpretation is outwith the scope of this work, the two sets of results clearly match well. The MATLAB script gives a slightly smaller shortest time constant and the DAS for this component agrees less well below 370 nm. These differences arise from the slightly different fitting procedure. Data are chirp corrected and the XPM removed prior to fitting data with MATLAB, whereas Glotaran fits them as part of the fitting procedure. This produces a slightly better fit at the shortest times, but Glotaran also takes significantly longer -
Figure 3.10: Results of fitting a three-exponential decay model to transient ellipticity data. (a) Decay associated spectra. The time-constant to which each spectrum corresponds is given in the legend. (b) Fits to several traces plotted as solid lines alongside measured data as dots.

The transient ellipticity spectrum shown in Fig.3.8 is well described by Eq.(3.3) with three exponentials with time constants of 1.7 ps, 120 ps and 1 ns and the gaussian IRF defined by $t_0 = 0$ ps and $\sigma = 0.27$ ps. Here the parameters defining the IRF are chosen manually to best describe the rise of the data. Reliable, quantitative errors on the fitting parameters could not be obtained for this fit, but changing the parameters by $\pm 5\%$ produces a noticeably worse fit. Since the maximum time-delay measured is 1 ns, decays with time constants several times longer than this show negligible change over the timescale of the experiment. They are reported by the fit as arbitrarily large time constants which behave as a constant offset to the signal. Parameters characterising the IRF are chosen to produce a suitable fit, rather than fitting them directly. This is because the IRF is more complicated than a gaussian, especially so when non-negligible XPM is present, as in this system. $t_0$ is therefore chosen to centre the decay-onset
around time-zero and $\sigma$ chosen to best represent the width of the IRF and the rise time of the signal, in this case it is the width of the probe pulse. This means that transient changes on similar timescales to the IRF cannot be reliably resolved since a bad fit at such times may be due to XPM rather than too few time-constants. With these approximations in mind, the DAS of this fit are shown in Fig.3.10 A. The DAS corresponding to 1.7 ps has two positive peaks around 1.8 and 2.2 eV whereas the 120 ps DAS has a broad negative peak around 2 eV. The 1 ns spectrum looks mainly like the 120 ps DAS but with a shoulder around 2.2 eV and a very shallow positive peak around 1.8 eV.

When fitting a kinetic trace to a sum of $n$ exponential decays, a parallel decay scheme model is implicitly assumed. This model states that there are $n$ independent excited states, each with different time constants, that decay straight back to the ground state. Therefore for a rearrangement of this decay scheme, each transient spectrum will be a linear combination of the DAS of the parallel decay scheme. [149] A monoexponential parallel decay scheme has little physical relevance in this system, where type II demagnetisation has previously been observed to be the major contributor to the TRMCD.[51, 52] Since there appear to be peaks from the 1.7 ps DAS in the 1 ns DAS, this component of the spectrum likely persists to much longer time-delays than the 1.7 ps time constant suggests and cannot be well-described by a single exponential. Species associated spectra are typically determined from a linear combination of the DAS by assuming that each decay pathway can be described by a monoexponential. However, the slow growth clearly cannot be expressed as solely a single exponential or even as a decay pathway so a different approach is needed. To extract the species associated spectra, an ansatz is made as to the form of the decay pathway. Therefore, Eq.(3.2) is changed to include a constant offset term, $c_i$, for each component

$$D_{fit}(\lambda, t) = \sum_{i=1}^{n} A_i(\lambda) \left( e^{-(t-t_0)/\tau_i} + c_i \right) \otimes \left( \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(t-t_0)^2}{2\sigma^2}} \right)$$

(3.7)

This only changes $C(t)$ and the constant offset accounts for the 1 ns term so only two components are needed. The spectra $A_i(\lambda)$ found from this model, called DAS for
simplicity, should therefore correspond to species associated spectra.

The DAS calculated by Eq.(3.7) and the corresponding decays are plotted in Fig.3.12, where a good fit is acquired with $\tau_1 = 1.7$ ps, $c_1 = 1.4$, $\tau_2 = 120$ ps, $c_2 = -2.1$. These two time-constants are the same as those found with Eq.(3.3) and the DAS look similar to those in Fig.3.10, suggesting that adding this constraint to the fit has minimal impact on the fitting parameters. Reliable, quantitative errors could not be obtained for these parameters but they are likely similar to slightly larger than those of the three-exponential fit. Spectrum $A_1$ has two clear peaks at 1.8 and 2.2 eV and decays quickly initially before plateauing and persisting to long times. In contrast, $A_2$ has one broad peak around 2.0 eV, which slowly grows to a long-lived plateau. The modified fit is slightly worse than the three exponential fit in Fig.3.10, yet still provides a good fit to the data. This difference is likely because a constraint has been added to the fit such that the spectrum is decomposed into only two spectra, effectively reducing the number of variable parameters. Furthermore, the assumption is made here that there are two processes occurring (the slow growth and the fast, but long-living decay) which can be described by an exponential plus a constant offset. Therefore, if there are other processes present or if an exponential and offset does not sufficiently describe the dynamics then the fit will be less accurate. Hence the fit has more physical relevance to the system at hand but relies on assumed constraints that could influence the subsequent results.

The slowly-growing component changes on a similar timescale to the previously observed type-II magnetisation dynamics in CGT. Type-II dynamics have an initial fast demagnetisation, followed by a significantly slower one. Fig.3.8 B shows a fast initial increase on the timescale of the pump as well, which is accounted for in the fit by the constant offset term. $A_2$ could therefore correspond to a slow demagnetisation of the system. If this is the case then $A_2$ should have a similar shape to the static ellipticity spectrum, albeit with opposite signal, since this spectrum is proportional to the magnetic field within the sample. While no such static spectrum could be measured for this sample, it has been calculated previously. [126] This calculated spectrum is plotted with $A_2$ in Fig.3.12 B, where it has been shifted by 0.4 eV such that the two
Figure 3.11: Modified two-exponential fit to transient ellipticity data at 20 K and 1.0 mJ/cm² plotted as (a) difference spectra at various time delays and (b) kinetic traces at various probe energies.

Figure 3.12: Decay associated spectrum from Eq.(3.7) applied to TRMCD data at various temperatures. (a) The quickly decaying component, $A_1$. (B) The slowly growing component, $A_2$. Also plotted is the ellipticity spectrum calculated by Fang et al. [126] for comparison.
spectra match relatively well. No other ellipticity spectra have been measured of CGT
and a 0.4 eV discrepancy between DFT computations and reality is plausible. [151]
The demagnetisation is also not-necessarily well-described by an exponential, since its
dynamics are often better described by more complex models. [31, 32] However, these
require too many unknown input parameters to be fitted accurately to our data for
the purposes of extracting the spectral components. The fit also does not account for
non-linear artefacts which may arise around time-zero, so this could be the cause of the
poor fitting at the very shortest times. Alternatively, there could be time-constants
faster than the temporal resolution of the measurement. This model is therefore used
as an approximation to the dynamics such that its spectral behaviour can be better
understood.

The two peaks in \( A_1 \) could correspond to transient carriers, since the photoexcited
carriers (both holes and electrons) will have different optical properties to their ground
state counterparts. Since there are no other allowed transitions accessible to 1.55 eV
light according to calculated DOS spectra, we believe that we are exciting spin-up
electrons across the band gap from the Te-5p valence band (VB) into the \((e_g - 5p)^*\)
conduction band (CB) of Cr character — a charge transfer transition [132]. We could
be pumping the higher-energy \( t_{2g} \rightarrow (e_g - 5p)^* \) transition, but this \( d-d \) transition will
be weakly dipole forbidden. However, both cases cause the occupation of the \((e_g - 5p)^*\)
orbitals with photoexcited electrons. By comparing to the calculated DOS from Fang
\textit{et al.}, [126] there are sharp spin-down peaks 1.8 and 2.2 eV above the CB minimum.
These peaks correspond to the spin-down Cr 3\( d \) orbitals and match well with the two
peaks in \( A_1 \). Equally, the peaks in \( A_1 \) could be due to photoexcited holes in the valence
band, but there are no peaks of the right energies in the valence band, regardless of
whether holes are generated in the \( t_{2g} \) or 5\( p \) orbitals. Regarding transient behaviour
of \( A_1 \), the signal shows a 1.7 ps initial decay to a long-lived plateau. This fast initial
decay could result from the relaxation of the photoexcited carriers back into the valence
band, since a similar fast time constant was observed for the \((e_g - 5p)^* \rightarrow 5p\) decay
in the closely related CST. [132, 141, 152] Previous studies of CST have also observed
an intermediate decay constant of around 20–40 ps, but this is neglected here to avoid
Chapter 3.2.2

3.2.2 Pump Polarisation Dependence

Right- and left-handed circularly polarised pump pulses were used to look for any helicity dependence to the TRMCD, like that observed in the Kerr rotation of CrI$_3$. Difference spectra at 200ps and traces at 2.0 eV and 1.8 eV are plotted in Fig.3.13. There is very little difference between the spectra. Small differences could be due to slight changes in alignment over the crystal or differences in the amount of light overfitting. Since these photoexcited carriers will be vibrationally hot, the temperature of the electron bath will rise. CGT has a small, indirect band gap so this increase in thermal energy can increase the equilibrium population of electrons in the CB until the heat is dissipated. This thermal increase in electrons in the $(e_g - 5p)^*$ orbitals can therefore account for the portion of $A_1$ which persists to long times. A small transient reflectance signal in CST was observed up to 5ns by Jnawali et al. which they assigned to the scattering of electrons to remote CB valleys. These electrons cannot recombine with VB holes without the mediation of a phonon so have a very long lifetime. This could provide an alternative explanation for the long-lived dynamics. Since both thermal and valley-trapping mechanisms result in an elevated CB carrier density, spectrum $A_1$ most likely arises from the ellipticity spectrum of photoexcited electrons in the CB.

Figure 3.13: Effect of pump helicity on the transient ellipticity at 20 K, shown as difference spectra at 2 and 200 ps. There is minimal difference between the two.
Temperature Dependence

Figure 3.14: Transient ellipticity measured using 1.0 mJ/cm$^2$ pump pulses and 2.0 eV probe at various temperatures.

scattered. Therefore it is difficult to make any conclusions over minor changes to the spectra and there is clearly no major change in magnitude or sign, as observed in CrI$_3$. Padmanabhan et al. [143] measured Kerr rotation while applying no external field, instead relying on the strong remanence of CrI$_3$. They attribute this to multiple domains in the pumped area, a minority of which will be antiparallel to the magnetisation. While our sample almost certainly has multiple domains, the applied field will saturate them. This results in a much smaller antiparallel minority, which is likely why no polarisation dependence is observed.

3.2.3 Temperature Dependence

Transient ellipticity spectra were also measured at several temperatures, using the same fluence, and these are plotted in Fig.3.14. The signal clearly decreases as temperature increases, but the dynamics remain similar between 20, 42 and 61 K. Spectral shapes also appear to be qualitatively independent of temperature, although the much lower signal-to-noise at higher temperatures makes this difficult. At 82 K, no long term growth in the signal greater than the noise is seen and it remains around 0 mdeg from 5 ps onwards. However, at shorter times a small positive signal is discernable above
Table 3.1: Fitting parameters for Eq.(3.7) applied to different temperatures. Errors on these values could not be obtained but the fits and data are plotted in Fig.6.1.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$\tau_1$/ps</th>
<th>$c_1$</th>
<th>$\tau_2$/ps</th>
<th>$c_2$</th>
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</thead>
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<td>20</td>
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<td>1.5</td>
<td>120</td>
<td>-2.1</td>
</tr>
<tr>
<td>42</td>
<td>1.9</td>
<td>1.4</td>
<td>130</td>
<td>-2.0</td>
</tr>
<tr>
<td>61</td>
<td>1.9</td>
<td>0.9</td>
<td>90</td>
<td>-1.7</td>
</tr>
<tr>
<td>82</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The noise which decays with a time constant of around 1.8 ps. Since this temperature is above the Curie temperature, the sample is expected to be paramagnetically, or very weakly ferromagnetically, ordered so no demagnetisation signal is likely to be observed. However, the photoexcited electrons are less dependent on long-range magnetic order and so it may be possible to observe their contribution to the transient ellipticity signal even when the material is no longer ferromagnetic. This is probably the origin of the portion of the signal that decays with a $\sim 1.8$ ps time constant.

To best understand these spectra, the modified global fit in Eq.(3.7) was applied to these spectra and the four parameters ($\tau_1, \tau_2, c_1, c_2$) are tabulated in Table 3.1. The signal-to-noise is not high enough for the 82 K spectrum for reliable global fitting so only an exponential fit was applied. Contour plots along with kinetic traces showing the fits at selected wavelengths are plotted in Fig.6.1. Error estimates for the fitting parameters could not be obtained, but there is a clear decrease in signal-to-noise as temperature increases. With this in mind, it cannot be claimed that there is any statistically significant temperature dependence of the fitting parameters from the dataset measured here. Magnetisation dynamics often change with temperature so some temperature dependence to the parameters would be expected, but here the noise in the data, few temperatures measured and lack of error bounds mean that such a dependence cannot be confidently observed.

The decay associated spectra, $A_1$ and $A_2$ are plotted for all three temperatures in Fig.3.12 A and B, respectively. Both spectra clearly decrease in amplitude as temperature is increased, albeit in a non-linear manner, and the shapes seem mostly independent on temperature. However, there appears to be a small red-shift of the quickly-
decaying peak at 2.2 eV at higher temperatures. The peaks are not well-described by typical lineshapes so shifts from around 2.17 eV at 20 K to 2.14 eV and 2.12 eV at 42 K and 62 K, respectively, were estimated by eye. The 1.8 eV peak might move to higher energies with temperature but is too noisy to tell. Watson et al. observed a +0.07 eV shift of the majority-spin \((5p - e_g)\) orbital in the valence band between 40 and 60 K using angle-resolved photoemission spectroscopy (ARPES). [121] This is much larger and in the opposite direction to the -0.02 eV we observed. They also observed a slight negative shift of the corresponding \(t_{2g}\) orbital. At higher temperatures, the ferromagnetic coupling in the material will be weaker, leading to a reduction in the energy difference between majority- and minority-spin states. Therefore, a positive shift in a majority-spin state will be accompanied by a negative shift of the minority-spin state, as we observe. Unlike ARPES, TRMCD can only probe transition energies rather than the relative energies of orbitals directly, so this could be the origin of the discrepancy between the magnitudes of the shifts.
3.2.4 Power Dependence

Transient ellipticity spectra were measured using two other pump fluences at 20 K and the kinetic traces and 2D spectra are shown in Fig.3.15 and Fig.6.1. The spectral shapes of the results are similar and have peaks in the same places, as is to be expected given that only fluence is changing. However, the transient behaviour is different. At longer times the highest fluence shows a slow growth characteristic of Type II demagnetisation, as discussed above. At the intermediate fluence the dynamics are similar but the growth is slower, taking almost twice as long to plateau. Finally, at the lowest fluence, the peak signal occurs immediately after photoexcitation, after which it decreases. On longer timescales the signal appears to grow again slightly however. This fluence dependence to the dynamics could be a result of a transition from Type II to Type I at lower fluences, as has been observed in several other materials previously, including CGT. [32, 51, 95, 136] Because of this change in the time-dependence, Eq.(3.7) no longer provides a good approximation to the data, so a meaningful global fit cannot be carried out without a more complicated time-dependence. However, qualitatively, the shapes of the spectra appear to vary little as power is changed, as can be seen in the contour plots in Fig.6.1.

3.3 Transient Transmittance

The transient transmittance, TT, was measured simultaneously with the transient ellipticity spectrum in Fig.3.16 and so also used a 1.0 mJ cm\(^{-2}\) fluence at 20 K. Again, the measurement was also repeated on the substrate, but no TT signal was observed here, except for XPM around time-zero. The results in Fig.3.16 are therefore due to the CGT itself, rather than the glass or metallic mask. There are three clear peaks, one negative at 2.2 eV, and two positive at 2.4 and 1.9 eV, with a small shoulder around 1.77 eV. From the contour plot, all these features persist to 1 ns with no drastic changes to the spectrum over time. The biggest change is the shift in the 2.2 eV peak by around 0.05 eV in the first 2 ps. This change is likely due to the growth of the 2.4 eV peak rather than a shift in energy of the 2.2 eV peak. The time dependence of selected probe
energies are plotted in Fig.3.17 B. For 2.00 and 2.21 eV, a fast initial decay followed by a slow growth to a long-lived plateau is observed. At 2.43 eV a fast growth to a long-lived plateau is observed instead, where the growth is likely due to the overlap of a quickly-decaying negative signal overlapping with a roughly constant positive signal. The trace at 1.82 eV shows less dynamics still, with a slight decay in the first few ps to a constant value out to 1 ns. Oscillations are visible across most of the spectrum up to 2 ps with a 0.3 ps period. Guo et al. observed two frequency components with 0.29 and 0.24 ps periods in the transient reflectance of CGT at 1.55 eV, resulting from the $A^1_g$ and $E^3_g$ Raman-active modes. [140] The $E^3_g$ mode was found to depend strongly on the presence of long-range magnetic ordering in the material and so results from spin-phonon coupling. The measurements reported here do not have the temporal resolution to resolve the two components from one another but the $E^3_g$ mode is much larger at 20 K so is the most likely contributor. Also, the differing experimental geometries could mean that transmittance spectroscopy can only measure one component.

The transient transmittance data were fit to Eq.(3.3) to better understand their dynamics. For the fitting procedure to converge on a physical result, the XPM had to be removed. Since it manifests as a large peak around time-zero, time-delays containing TT above a certain threshold within a picosecond of time-zero were excluded from the
Figure 3.17: Results of a three-exponential global fit to the transient transmittance at 20 K using 1.0 mJ/cm². A) Decay associated spectra. B) Kinetic traces at various probe energies, with the fit shown as solid lines.

fit. As can be seen from the kinetic traces in Fig.3.16, the XPM is clearly larger than and distinguishable from the TT itself. However, by excluding the XPM rather than removing it, the fit cannot accurately account for behaviour on the timescale of the XPM itself. Therefore a lower bound of around 200 fs was set for the time-constants.

The data are well-described by a three-exponential fit, Eq.(3.3), with time constants \( \tau_1 = 1.7 \) ps, \( \tau_2 = 80 \) ps and arbitrarily large \( \tau_3 \). The DAS corresponding to \( \tau_3 \) has a broad negative peak in the red and a smaller one around 520 nm, with positive peak in between, almost like a second derivative. The broad, red peak is also present in the \( \tau_1 \) spectrum, except the spectrum is more like a first derivative, with only a positive peak at the blue end. Since it corresponds mainly to a growth of the signal, the second, \( \tau_2 \), DAS appears almost intermediate between the other two DAS but inverted. It is also much smaller, reflecting the relatively small magnitude of the slow growth of the signal.

Clearly, \( \tau_1 \) is similar to the shortest time constant in the TRMCD, which could suggest that the same process is responsible for both decays. In contrast, \( \tau_2 \) is quite different to the 120 ps observed in the TRMCD so likely does not arise from directly the same mechanism. Both TRMCD and TT have a signal which decays on much longer times than the experiment. The respective agree- and disagreement of \( \tau_1 \) and \( \tau_2 \) fit within the model proposed above however. If the photoexcited electrons have a contribution to the TRMCD then they will likely have a contribution to the TT.
as well, whereas the demagnetisation would be expected to only significantly affect the TRMCD. The fast component of the TT could therefore arise from a combination of excited state absorption and ground state bleach caused by these photoexcited electrons. This of course assumes that the dependence on the TT has the same dynamics as the TRMCD, which is not necessarily true if the TT signal arises from a many-body phenomenon. The most likely such effect, band gap renormalisation, results from the perturbation of the electronic structure by the transient carriers. Band gap renormalisation is common in ultrafast spectroscopy of semiconductors, has a cube root dependence on the carrier density [153] and manifests as a red-shift of transition energies. [28] Additionally, as with the TRMCD, processes within the material can only be accurately described by a continuous and time-dependent distribution of time-constants, which is almost impossible to fit without significant a priori knowledge of the system. However, single exponentials can still provide a sufficient approximation.

Assigning features in the TT is difficult given only the measurements taken in this experiment. If the sample were instead molecules in solution, then the spectrum could be interpreted as excited state absorption superimposed over ground state bleach. However, since the sample is a crystal, other transient phenomena are possible. Ground state bleach instead manifests as a blue-shift of transition energies as the carriers close to the band edge are excited first.[29] This is most prominent in TT spectra of semiconductors around the band gap, but is observable at all transition energies. These measurements were taken well above the 0.7 eV band gap and there are no notable transition peaks in the absorption spectrum within the region probed at high temperature. However, other transitions above the band gap may be possible at low temperature, and a shift in their energies could result in the derivate-like shape of the TT spectrum. Shifting of bands on the timescale of the experiment is modelled poorly by Eq.(3.4), which assumes that the DAS are time-independent. No peaks appear to shift in Fig.3.16, so a bilinear model is still likely applicable.

The most likely cause for the long-lived signal is heating of the sample by the pump pulse. Thermal effects often dominate transient absorption spectra of thin film semiconductors at long times. [28, 29, 154, 155] Cooper et al. measured transient
absorption of 50 nm thick BiVO$_4$ and, through careful analysis, found that the dynamics in the initial 10 ps were due to hot photoexcited carriers manifesting as band gap renormalisation and free carriers. [28] However, at longer times, the majority of the transient absorbance was because of thermal effects, and the thermal contribution grew over the course of 200 ps as the electrons thermalised with the lattice. They showed this by measuring the change in static absorbance as the sample was heated, which looked little like the static spectrum but matched almost exactly their transient absorption signal, allowing them to estimate the temperature rise of the sample. CGT is a poor thermal conductor [156] in the $a - b$ plane, and even worse along the $c$-axis. This anisotropy is typical of layered materials, where thermal conductivity is typically $\times 100$ larger in-plane than out-of-plane. Sun et al. observed a long-lived signal in the transient reflectivity of CGT, which they assigned to heating. To support this, they carried out heat transport simulations of a thermally anisotropic material and found that there was minimal diffusion of heat below a nanosecond. In our case, the pump pulse is also larger than the crystal so it is almost homogenously excited in the $a - b$ plane but will initially have an exponential temperature gradient along the $c$-axis. Therefore the in-plane direction will come to thermal equilibrium much faster than the out-of-plane direction, yet heat must propagate along this axis in order to diffuse into the substrate and dissipate. Based on the low thermal-conductivity and the similar lattice-electron thermalisation times in BiVO$_4$, $\tau_2$ likely corresponds to the transfer of energy from the photoexcited carriers into the lattice. However, to show this for sure, more careful measurements of the temperature dependence of the absorption spectrum are needed, to confirm if they have the same shape as the thermal contribution to the TT spectrum.

### 3.3.1 Temperature Dependence

Transient transmittance spectra were measured at several temperatures and then fitted to a three exponential global fit, in the same manner as Fig.3.17. Contour plots for each temperature except 20 K are shown in Fig.6.2. The TT decreases as temperature increases, but without higher resolution temperature dependence, it is difficult to tell
Temperature Dependence

Figure 3.18: Temperature dependence of the decay associated spectra resulting from fitting a three exponential global fit to TT spectra pumped with 800 nm, 1.0 mJ/cm² pulses.

The mechanism for this. CGT is known to have a kinks in its heat capacity and thermal expansion coefficient around $T_C$ due to strong spin-phonon coupling. [157] Therefore, if the TT arises from thermal effects then this will have a non-trivial temperature dependence. The decrease in TT could also be due to a greater carrier density at higher temperatures because of the small band gap. Photoexcited carriers would be a much smaller proportion of the total charge carriers which could in turn reduce the TT signal. The time constants of the fit did not have any clear temperature dependence, suggesting that the dynamics are mostly temperature independent. However, at higher temperatures, the signal-to-noise gets smaller, so there may be temperature dependence below our noise level.

The fastest component of the DAS, roughly retains its shape as temperature increases, with a negative peak around 2.3 eV and a positive peak around 1.9 eV. As temperature increases, both features decrease and a broad negative feature towards the infrared appears to grow. Free, Drude-like, carriers in a material often manifest as a negative signal which grows towards the infrared in TT spectra. [28] This temperature dependence could therefore show the reduction of the signal from photoexcited carriers and the growth of a signal from free carriers as temperature increases. However, this
is speculative, and more careful measurements would be needed to confirm this.

Slow growth in the TT spectrum is much smaller than the fast decay or the long-lived state, as shown by the small magnitude of the intermediate component in Fig.3.18. An 80 ps growth is only visible at 20 K and 42 K, but again at the higher temperatures, it could well be below the noise level, so it is difficult to draw any conclusions from this. However, if this component arises from electron-lattice thermalisation, then a temperature independent $\tau_2$ could suggest a temperature independent electron-phonon coupling, which is expected for semiconductors. [152]

Finally, the longest component shows the most straightforward temperature dependence with all features decreasing as temperature increases. That said, the thermal expansion and heat capacity of CGT become larger as temperature tends towards $T_C$. [157] All measurements in Fig.3.18 used the same fluence and so deposited the same energy into the system. Therefore, as initial temperature increases, the pump-induced rise in temperature of the material will be smaller, so this may cause a smaller thermal contribution to the TT. However, without more evidence that heating causes this long-lived feature in the spectrum, it is difficult to make concrete statements about the temperature dependence.

### 3.3.2 Power Dependence

Much like the TRMCD described above, power dependence of the TT signal was also measured at three different pump powers, plotted in Fig.6.3. All were measured at 20 K with 1.55 eV pump pulses. It is expected that the TT will increase linearly with pump power so this has been plotted in Fig.3.19 for several time delays and wavelengths. A linear fit which passes through the origin is included on each plot as a guide to the eye since no fluence should correspond to no change in transmittance. There is an approximately linear dependence at all nine points in the TT spectra, showing that the pump pulses are still within the linear regime for the system, although this is less clear for longer times at 2 eV. However, given that there is only data for three fluences, it is difficult to say this with any certainty, except that an increase in power corresponds to an increase in signal for the three powers measured. Curvature in this dependence
Figure 3.19: Power dependence of TT signal at 1, 10 and 100 ps and at 560, 620 and 700 nm (2.21, 2.00, 1.77 eV), measured at 800 nm. A line-of-best-fit which passes through the origin is also shown, as a guide to the eye.
could mean that non-linear optical processes are happening within the system, such as two-photon absorption, or even just that the response saturates at higher powers.

That it appears linear at 1 ps when the signal from photoexcited carriers dominates suggests that band gap renormalisation is not the mechanism behind $\tau_1$.

Unlike the TRMCD, from looking at the raw data, the dynamics of the TT do not change dramatically with power, although the slow rise does appear to become faster at lower powers. They could therefore be fit with a three exponential model using Eq.(3.2). The results of this for each fluence are plotted in Fig.3.20 and the corresponding parameters in Table 3.2. Given the lack of errors here, few concrete conclusions can be made from the fitting parameters themselves. The longest time constant is arbitrarily large for all powers and the shortest shows no clear dependence on power. This matches the dependence of $\tau_1$ on power seen in the TRMCD data. However, $\tau_2$, the intermediate time constant, appears to decrease as power increases, something that can also be seen in the raw data. If this component is indeed due to thermalisation, then this dependence could be due to a complex dependence of the thermal transport on temperature. From the DAS, the longest component appears to increase roughly linearly with power and has pretty much the same shape for each
Air Sensitivity

<table>
<thead>
<tr>
<th>Power /µW</th>
<th>$\tau_1$ /ps</th>
<th>$\tau_2$ /ps</th>
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<tbody>
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Table 3.2: Fitting parameters for Eq.(3.3) applied to transient transmittance spectra at different pump powers. $\tau_3$ is arbitrarily large for all three powers so is neglected.

The shortest component has a similar magnitude to the longest DAS, but the shape changes with power. Most notably, the large negative peak around 1.9 eV is not present at the lower powers. This spectral dependence on power could be because the dynamics change subtly and no longer conform to Eq.(3.2). This limits the applicability of the multiexponential fitting model to this dataset. However, features in transmittance spectra are notoriously hard to assign, especially when there is scant other data to compare to (e.g. static spectra or time-dependent calculations).

3.4 Air Sensitivity

Following the measurements above, sample A was stored in a glovebox, under what was intended to be a nitrogen atmosphere. After a month in storage, transient absorbance and ellipticity were measured at 20 K using 1.0 mJ/cm$^2$ pump. A comparison of the difference spectra at 200 ps measured in February and March is plotted in Fig.3.21. The ellipticity has clearly decreased in magnitude by about half but the shape is the same, with the peak at 2 eV and a shoulder around 2.3 eV. In contrast, the shape of the TT has changed to almost exclusively ground state bleach. There is still a large peak around 1.9 eV but it is narrower and the derivative shape centred on 2.3 eV has almost disappeared completely.

A second sample, B, was also measured at low temperature with both old and new setups. It has the same structure as sample A but the crystal is wider and it had been stored in the glovebox for longer initially than sample A. The TT and TRMCD were measured following 800 nm, linearly polarised, $\sim$3 mJ/cm$^2$ photoexcitation at 20 K and the TT is plotted in Fig.3.22. Since this was measured with white light generated
Figure 3.21: Transient (a) ellipticity and (b) transmittance spectra at 200 ps measured under the same conditions for sample A, but one month apart.

Figure 3.22: TT spectrum of sample B at 20 K following 800 nm, ~3 mJ/cm² photoexcitation. (a) Contour plot to 50 ps. Note that all signal, excluding XPM, is positive. (b) Kinetic traces at selected wavelengths. (c) Difference spectra at selected times.
Air Sensitivity

Figure 3.23: Effects of suspected oxidation on the TT spectrum. (a) TT spectrum of sample C at 20K. (b) TT spectra of sample B at 150 ps, measured four months apart.

in sapphire by 800 nm pulses, it extends slightly further into the blue. It looks very different to the spectrum measured for sample A in Fig.3.16 with only monotonically-decaying signal of a single sign visible. Three peaks also persist to long times at 475, 600 and ~740 nm.

TT was also measured at 20 K for a third sample, C, for which no TRMCD signal could be measured. This spectrum, plotted in Fig.3.23 A, shows only positive transmittance change which is larger towards the red, with no peak around 600 nm. Since sample C was much larger than sample B and could be a different thickness, the TT cannot be compared directly, but this spectral difference is clear.

Four months later, in October, the measurements were repeated. In between, the sample was stored in a glovebox under what was intended to be a nitrogen atmosphere. To obtain a measurable ellipticity change, the measurements in October were carried out at 13.5K. However, the different shape of the TT meant that the fluence could not be matched exactly to the fluence used in June. During alignment, it was observed that only the size of the TT spectrum changed changing the pump fluence, whereas the shape remained roughly constant. The difference spectra at 150 ps measured in June and October are compared in Fig.3.23 B. They are clearly different. The slightly narrower white light used in October is responsible for the loss of the 475 nm peak. However, the peak at 600 nm decreased dramatically over time.

The TRMCD spectra at 150 ps and kinetic traces at 150 ps are plotted in Fig.3.24A
Figure 3.24: Magneto-optical spectra for sample B, measured in June and October. (a) Difference spectra at 150 ps. (b) Kinetic traces at 2.0 ev.

and B, respectively. All are clearly very noisy but there is structure visible in the TRMCD from June, with a small positive signal below 1.9 eV, a broad positive peak around 2.2 eV and a crossing of zero around 2.5 eV. The spectrum is similar to Fig.3.8 but is much smaller. This signal also slowly grows over the course of several hundred picoseconds, in common with the dynamics observed in sample A. Also like sample A, saturation ellipticity could not be measured so the results could not be converted into a proportional change in magnetisation. The TRMCD has clearly decreased in size between the two measurements, but has very similar shape. The dynamics are too noisy to draw many conclusions from, except that the TRMCD does not appear to change significantly with time-delay. This change in shape of the TT but not the TRMCD observed in both samples A and B is indicative of a physical change to the material. If the composition of some of the material has changed — e.g. through formation of an oxide layer — then the new material is most likely non-magnetic but will probably still show some TT. This would result in a different overall TT spectrum, but would merely reduce the size of the TRMCD signal.

3.5 Conclusion

CGT is a promising material for magneto-optical studies of magnetic semiconductors at the 2D limit because its magneto-optical properties show a strong dependence on probe wavelength. Here, I have showed that using a broadband probe technique allows
us to split the spectrum into its contributions from photoexcited electrons and demagnetisation. At 20 K using 1.0 mJcm$^{-2}$ pump pulses, a 1.8 ps fast decay and a 120 ps slow growth could be observed in the transient ellipticity spectrum. This slow growth had previously been observed and assigned to type II demagnetisation but the fast decay had not been reported in the literature previously so merited further exploration. A global fit was applied which took this slow growth behaviour into account to extract the spectra which corresponded to the fast decay and slow growth dynamics. The slowly growing spectrum had a similar shape to calculations of the static ellipticity, as would be expected for demagnetisation. In contrast, the other spectrum had a very different shape and dynamics, consisting of two peaks centred on 1.8 and 2.2 eV which decay quickly immediately but persist to longer times. Through comparison to previously calculated density of states spectra, the positions of these peaks were found to match well with transitions of photoexcited carriers from excited ($e_g - 5p$)$^*$ orbitals to minority spin Cr-3$d$ orbitals. With this interpretation, the broadband TRMCD technique has been used to measure the excited state ellipticity spectrum and track the dynamics of the photoexcited carriers. A monochromatic probe could have misinterpreted these two contributions to the transient ellipticity as both arising from demagnetisation. Furthermore, a broadband approach allows for more detailed picture of the electronic structure in this case. Temperature and fluence dependencies of the spectrum were also investigated. As would be expected, demagnetisation was only observed below $T_C$. The dynamics of the contribution from photoexcited electrons appeared to show different fluence and temperature dependence to the demagnetisation and were still visible above $T_C$. However, measurements of the temperature and fluence dependencies were limited by a low sample size and a low signal-to-noise at high temperatures and low powers. Higher quality measurements at a greater number of temperatures and fluences would give a much clearer idea as to these dependencies.

Simultaneously, TT spectra were also measured, which corroborated the TRMCD measurements. A large, long-lived component in the TT was also tentatively assigned to heating of the sample. To fully characterise the TT spectra, careful measurements of static and low temperature absorption and refractive index spectra are likely needed.
Finally, the measurements were made more difficult by the strong air sensitivity of CGT, which changed the TT spectrum and reduced the TRMCD signal upon oxidation.
Chapter 4

Magnetic Circular Dichroism
Spectroscopy of Excited States of Zinc Tetrphenylporphyrin

Metalloporphyrins find countless applications across photochemistry and photophysics. They are large, conjugated molecules that, at their simplest, consist of a planar ring of many carbon and nitrogen atoms which form a chelating ligand around a central metal ion. Because of the large conjugated structure causing fully allowed $\pi - \pi^*$ transitions, they absorb UV and visible light very strongly. Arguably the two most familiar metalloporphyrins are chlorophyll and heme. The former has manganese at its centre and its large absorption coefficient in the blue and red makes it ideal for photosynthesis in plants. The latter contains an iron ion, is strongly red-coloured and is responsible for carrying oxygen in the bloodstream, making it a major constituent of hemoglobin. A great strength of porphyrins is that, provided the constituent ring is preserved, a vast number of functional groups can be attached to tweak the molecules properties in predictable ways.[158, 159] This is of course widely utilised in nature with the structures of both heme and chlorophyll varying greatly depending on the reaction system they are used within. Because of their strong optical absorption, potential for tunability and great importance in biological chemistry, they are among the most intensively studied classes of chromophores.
Naturally occuring porphyrins are often complex with large numbers of asymmetrically-attached functional groups. Therefore, model porphyrins with few or symmetrical functional groups are often studied initially to best understand their properties, before adding groups to tailor the molecule to a particular purpose. Zinc meso-tetraphenylporphyrin (ZnTPP) is one such model porphyrin, whose structure is shown in Fig. 4.1. It consists of four phenyl groups distributed around a porphyrin ring which is bound to a Zn$^{2+}$ ion at the centre. The Zn has been shown to lie very slightly above the porphyrin,[160] but the molecule is effectively planar with $D_{4h}$ symmetry. The excited states of ZnTPP and its derivatives vary predictably across functional groups and environments,[159] making it ideal for use in many applications. It has therefore previously been used in quantum logic gates,[161] light harvesting antennae,[80, 162] photosensitizers for photodynamic therapy,[163] and sensors [164]. Transient methods like TA and TRMCD are ideal for direct measurements of excited states so could provide more details as to the electronic structure of the excited states. Broadband TRMCD on picosecond timescales has yet to be measured for any molecules and ZnTPP is an ideal system to explore with this new method.

The aim of the work presented in this chapter is to measure and understand the TRMCD spectrum of ZnTPP. To interpret the TRMCD, one first has to interpret the
ZnTPP Background

Figure 4.2: Ground-state absorption and static fluorescence spectra of 0.12 µM ZnTPP in benzene, from Ref.[165]. Excitation wavelength for the fluorescence was 397 nm.

static MCD spectra and therefore the electronic structure of the molecule must first be known. The first section of this chapter therefore introduces what is already understood regarding the electronic structure, absorption spectrum and transient behaviour. Following this, measurements of the static MCD and transient absorption are presented and used to assign features in the TRMCD.

4.1 ZnTPP Background

The absorbance spectrum of ZnTPP in benzene is shown in Fig.4.2, reproduced from Ref.[165]. It has two main features: a very intense peak at 423 nm, called the Soret or B band, and a weaker peak at 549 nm, called the Q band. Both B and Q peaks are present in almost all porphyrinoid absorbance spectra, something which has been known since the early 1900’s.[166] However, they could not be confidently assigned to any particular transitions until the 1960’s.[158] There are also various side peaks at 402, 510 and 589 nm which will be discussed in due course.

Without the Zn$^{2+}$ ions, nitrogen atoms and phenyl groups, ZnTPP is effectively a
cyclic $C_{16}H_{16}^{2-}$ ion, something which is much simpler to model. By considering linear combinations of the carbon $p_z$ orbitals, one can determine the form and ordering of the $\pi$ molecular orbitals ($\pi$-MOs) of the system based on their orbital angular momentum quantum numbers, $M_L$. The most important of these orbitals are the frontier orbitals, which are formed out of the $1e_{4u}$ and $1e_{5g}^*$ MOs and have $M_L = \pm 4$ and $\pm 5$, respectively.[21] In the ground state $1e_{4u}$ is fully occupied and $1e_{5g}^*$ is empty so they act as the HOMO and LUMO. Transitions from $1e_{4u} \rightarrow 1e_{5g}^*$ can therefore either have a change in one quantum of angular momentum ($\Delta M_L = \pm 1$) or nine ($\Delta M_L = \pm 9$). This scheme is shown in Fig.4.3(a), where each MO is labelled by its $M_L$ number. Under the dipole approximation, only transitions of $\Delta M_L = \pm 1$ are allowed. The forbidden $\Delta M_L = \pm 9$ transition will also be of lower energy because of Hund’s second rule that the lower energy states are those with greater angular momenta. Thus one can make the tentative assignment that the strong B band is due to the allowed $\Delta M_L = \pm 1$ transitions and the weak Q to the forbidden $\Delta M_L = \pm 9$.[158]

Almost all of the $\pi$-MOs for the pure $C_{16}H_{16}^{2-}$ ion are doubly degenerate on account of the high symmetry. $C_{16}H_{16}^{2-}$ is of $D_{16h}$ symmetry whereas ZnTPP is of $D_{4h}$. As the symmetry is reduced from $D_{16h} \rightarrow D_{4h}$, the degeneracy of some of these MOs is lifted. Thus the $1e_{4u}$ becomes $1a_{1u}$ and $1e_{2u}$ and the $1e_{5g}^*$ becomes a $1e_{g}^*$. Importantly, both $1a_u$ MOs have partly $M_L = -4$ and $+4$ character. Although the $\Delta M_L = \pm 9$ transition is forbidden, mixing between the states makes it weakly allowed, resulting in the strong
absorbance seen in Fig.4.2. This model which considers only the four frontier MOs was developed by Gouterman [158] and has shown considerable success in explaining and predicting the properties of visible absorbance spectra of porphyrinoids.[167] The excited states proposed by Gouterman of this general system are shown in Fig.4.3b. Exciting the B band corresponds to the $S_0 \rightarrow S_2$ transition and the Q band corresponds to the lower energy $S_0 \rightarrow S_1$ transition. Both excited states are singlets with two-fold degeneracy. In the ground state, $S_0$, both $1a_{1u}$ and $1a_{2u}$ are fully occupied so the spin quantum number of this system is $S = 0$ and $S_0$ is non-degenerate.

The main success of Gouterman’s model was deriving simple expressions for the energies of the B and Q bands in terms of the energies of the $1e^*_g(\pi^*)$, $1a_{1u}(\pi)$ and $1a_{2u}(\pi)$ MOs. Changing the ring substituents, the character of the central metal ion and the axial functional groups changes these energies in a predictable manner. For example, only the $1a_{2u}$ MO has electron density at the meso positions of the ring. Therefore adding meso-phenyl substituents to the porphyrin, as in ZnTPP, raises the energy of the $1a_{2u}$ relative to the $1a_{1u}$ MO. Likewise, adding functional groups to the exo positions of the ring will instead affect the $1a_{1u}$ MO. If the symmetry remains $D_{4h}$, or axial ligation reduces it to $C_{4v}$, the symmetry classes of these four MOs remain the same. Adding groups asymmetrically to the porphyrin ring, as is the case for biologically occurring porphyrinoids like heme and chlorophyll, lifts the degeneracy of the LUMO. This gives both Q and B bands electronically allowed character, resulting in much higher absorption from the Q band. Although ZnTPP has $D_{4h}$ symmetry, the size of the splitting between the $1a_{1u}$ and $1a_{2u}$ MOs is on the order of 0.05 eV making them almost degenerate.[21, 168]

With Gouterman’s model in hand, the absorbance spectrum of ZnTPP shown in Fig.4.2 can finally be explained. The Zn$^{2+}$ ion at the centre of ZnTPP has fully occupied $d$-orbitals so $d-d$ transitions will not contribute to the absorbance spectrum. Furthermore, charge transfer transitions between the metal and ligand are not observed within the 300-800 nm spectral range of typical UV-visible spectroscopy. To identify these peaks, the fluorescence spectrum of ZnTPP is needed - plotted as a dotted line in Fig.4.2 following 397 nm excitation. It has peaks at 428, 596 and 645 nm and the
highest energy fluorescence is due to relaxation from the $S_2$ state. The transitions in Fig.4.2 can be labelled by the number of quanta in the dominant Frank-Condon active vibrational mode in the excited and ground states, respectively. In the ground state, all molecules are assumed to occupy the vibrational mode of lowest energy. There is a peak in the fluorescence spectrum at 596 nm, which corresponds to the 589 nm transition in the absorbance spectrum. These are assumed to be due to the $Q(0,0)$ transition, with a Stokes shift of 80 cm$^{-1}$ ($\sim 0.01$ eV) and a centre of 16,700 cm$^{-1}$ (2.09 eV). By converting differences in wavelength to differences in energy, the larger peaks at 549 and 645 nm are found to lie 1,400 cm$^{-1}$ (0.17 eV) above and below the centre of the $Q(0,0)$ transition, with a peak at 510 nm 2,700 cm$^{-1}$ (0.34 eV) above. Therefore, with the assumption that 1,700 cm$^{-1}$ (0.17 eV) corresponds to the difference between the dominant vibrational modes, they are labelled as the $Q(2,0)$, $Q(1,0)$ and $Q(0,1)$ transitions in descending energetic order. In a similar manner, the peak in the absorbance spectrum at 423 and fluorescence and 428 nm, are assigned to the $B(0,0)$ transition. The shoulder at 402 nm also lies 1,700 cm$^{-1}$ (0.17 eV) above the centre of the $B(0,0)$ transition and is thus assigned to the $B(1,0)$ vibronic transition.

4.1.1 MCD Spectroscopy

In addition to strong absorption and fluorescence spectra, porphyrinoids also show strong MCD spectra,[24, 169, 170] and ZnTPP is no exception to this. From the states in Fig.4.3(b), the ground state is non-degenerate but both excited states are doubly degenerate. Therefore, when a field is applied, this degeneracy is lifted and $S_1$ and $S_2$ states split into two sublevels each. This is the typical system shown in Fig.1.2 for $A_1$ terms. From the structure in Fig.4.3(b), one would expect two $A_1$ terms, centred on the $B(0,0)$ and $Q(0,0)$ transitions. However, as the $S_0$ state is formed out of the non-degenerate $1\alpha_{1u}$ and $1\alpha_{2u}$ MOs, the analysis of this becomes more complicated as the relative energies of all frontier orbitals and their mixing must be taken into account. Because of this, small $B_0$ terms are also expected. This is exactly what is observed for ZnTPP in toluene and benzene, except there is also an $A_1$ term observed centred on the $Q(1,0)$ term.[171–174] There are also many vibronic transitions in the absorbance
spectrum which add small contributions to the MCD. Because this requires much more complex analysis of the symmetries of the vibrational modes,[20] such transitions are beyond the scope of this work, which will mainly focus on the Q(0,0) contribution to the MCD. As all the states are singlets, \( S = 0 \), it can be shown that \( \mathcal{A}_1/D_0 = \mu_z \). Therefore, the magnetic moment for the excited state can be determined from comparison of absorption and MCD spectra. For the Q(0,0) band, \( \mu_z(S_1) = 2.48 \mu_B \) and 3.52 \( \mu_B \) in benzene and toluene, respectively, and \( \mu_z(S_2) = 0.73 \mu_B \) in benzene for the B(0,0) band.[172, 173] Considering the electronic structure from simpler models, such as through the movement of individual electrons between MOs, results in magnetic moments of \( \mu_z(B(0,0)) = 1 \mu_B \) and \( \mu_z(Q(0,0)) = 9 \mu_B \).[24] In light of the MCD-calculated values, the four-orbital model, which allows for a much greater variance in the magnetic moments, is a more accurate model of the system. MCD spectra are typically very difficult to model accurately, and ZnTPP is no different, with computational studies proving largely inaccurate for predicting or reproducing the spectrum.[175] Because of this, there still exists significant uncertainty in the values of the magnetic moments.[21]

### 4.1.2 Transient Absorption

Because of the aforementioned rich ground state spectroscopic properties of ZnTPP, it has also been the subject of much transient spectroscopy to probe the excited states and their lifetimes.[165, 177, 178, 180–190] The generally accepted picture of the spectroscopic excitation is shown in Fig.4.4. Excitation of the B band causes an \( S_0 \rightarrow S_2 \) transition. If the blue side of this transition is pumped (e.g. \(<420 \text{ nm}\) ), then the molecule ends up in a vibrationally hot \( S_2 \) state and subsequently undergoes vibrational cooling (VC) The VC was initially assigned to internal conversion (IC) from a higher lying singlet state down to the \( S_2 \) state,[165] yet more recent four-wave mixing experiments by Abraham et al. proved this to be false.[180] They found a time-constant for the relaxation in tetrahydrofuran after 420 nm excitation of 70 fs. Once in the \( S_2 \) state the molecules can undergo radiationless decay via IC into the \( S_1 \) state. This typically takes place with a time-constant around \( \tau_1 \sim 1.5 \text{ ps} \) in benzene and toluene.[165, 178, 180] Additionally to this, fluorescence is also observed from the \( S_2 \rightarrow S_0 \) relax-
Figure 4.4: Relaxation pathway of ZnTPP in toluene/benzene following 400 nm excitation to the $S_2$ state. The initial photoexcitation is denoted by a dashed arrow and fluorescence by dotted arrows. Vibrational cooling (VC), internal conversion (IC) and intersystem crossing (ISC) drive non-radiative decay and are shown by solid arrows. Each decay process is labelled with their respective time constants. The respective origins of all values are given in more detail in the main text.[165, 176–180]
Transient Absorption, as shown in Fig. 4.2, yet it is much weaker than the $S_1 \rightarrow S_0$ fluorescence with a quantum yield of less than $10^{-3}$.

Since $S_2$ lies much higher in energy than $S_1$, the molecule then undergoes further vibrational cooling to the bottom of the $S_1$ state. The vibrational cooling does not cause a large change in the TA spectrum but instead slightly narrows and blue-shifts the peaks. Therefore, the signature of vibrational cooling in the TA spectrum is often subtle and harder to quantify, and the spectral features associated with it do not lend themselves to fitting with exponentials. With this in mind, the relaxation is typically on the order of $\sim 10$ ps.[165] Once in the $S_1$ state, the photoexcited molecules then undergo intersystem crossing (ISC) to the $T_1$ state. The population of the $S_1$ state decreases with a time-constant of $\tau_2 \sim 2.0 \pm 0.2$ ns.[177] However, not all molecules in the $S_1$ state decay by ISC, some relax directly into $S_0$ through fluorescence or non-radiative IC. The quantum yield of the $S_1 \rightarrow S_0$ non-radiative IC is $\sim 0.1$.[177–179] Since ZnTPP gives off strong fluorescence from the $S_1$ state, it is frequently used as a standard reference measurement for fluorescence spectroscopy. By comparing the values measured by a large number of papers from 1940–2020, Tanaguchi et al. found a reliable value of $\phi_F \sim 0.030$. In the relaxation pathway in Fig. 4.4, this quantum yield corresponds to the proportion of molecules which undergo fluorescence rather than ISC or IC. Therefore the corresponding time constant is $\tau_{F,1} = \tau_2 / \phi_F$. The same process can be carried out for the $S_2$ fluorescence and the $S_1$ IC. Given the quantum yields of fluorescence and IC from the $S_1$ state, it follows that the proportion of molecules that undergo ISC is $\sim 0.87$. Thus all relevant time constants in Fig. 4.4 are found.

Finally, the molecules in the $T_1$ state relax by phosphorescence back into the $S_0$ state with a typical time constant of 1-2 ms. The energy of the $T_1$ state relative to $S_0$ can be determined from this phosphorescence.[176] This time constant increases greatly in degassed solvents or at low temperatures.[177] However, given that it is six orders of magnitude beyond the capabilities of our setup, a detailed discussion of the phosphorescence is beyond the scope of this study. However, as the phosphorescence time-constant, $\tau_P \sim 1$ ms, is of a similar size to typical pulsed laser repetition rates of $\sim 1$ kHz, care must be taken not to excite molecules already in the triplet state.
The meta-analysis of Taniguchi et al. [177] discussed the solvent dependence on the static and transient properties of ZnTPP. They found that there is minimal dependence of the parameters they investigated on solvent, especially between toluene and benzene, which are the two most common solvents used with ZnTPP. For ZnTPP there is also little dependence of the fluorescence on the presence of dissolved oxygen, which can often quench fluorescence. Certain solvents may form axial ligands with the Zn ion but this is not the case for toluene and benzene, and they found no statistically significant difference in spectroscopic parameters between the two. However, they note that the presence of impurities can skew fluorescence measurements. Most common for ZnTPP is its more-fluorescing precursor, H$_2$TPP ($\phi_F \sim 0.08$, $\tau_{ISC} \sim 13$ ns). The only exception to the lack of solvent dependence is the energy difference between the $S_2$ and $S_1$ states.[168] This effect is small and has a clear and predictable dependence on the solvent used, with benzene and toluene having almost identical effects.

Previous transient absorption measurements of ZnTPP in toluene or benzene find that the spectrum has contributions from ESA, GSB and SE for excitation of both B and Q bands. [165, 178, 180, 191] As one would expect, the GSB and SE have similar shapes to the static absorbance and fluorescence spectra. A broad featureless ESA is present at all time delays, making it difficult to distinguish features of the difference states. However, there are clear ESA peaks in the near IR corresponding to $T_1 \rightarrow T_n$ and $S_1 \rightarrow S_n$ transitions at 850 and 1250 nm, respectively. [178, 191] Computational results suggest that there are many closely spaced states above $S_1$ [168] whose overlapping absorption peaks could appear like transitions into a continuum in electronic spectroscopy, resulting in a rather featureless ESA. The energy differences between the lowest of these states and $S_1$ or $T_1$ are around 8,000 – 12,000 cm$^{-1}$ (1 – 1.5 eV), hence the peaks in the near IR ESA.

All of the measurements described in this thesis use ZnTPP dissolved in toluene at room temperature. The compound was bought from Sigma Aldrich and has a purity of $\geq 97.5\%$. Static measurements done to characterise the compound are described first, after which the results of the transient experiments are shown. Transient absorbance and time-resolved magnetic circular dichroism were measured simultaneously, but are
4.2 Static Characterisation

ZnTPP has a characteristic UV-Vis spectrum and has been observed to aggregate at relatively low concentrations in specific solvents, such as in methylsulfoxide with 1% water.[177, 192] Absorbance typically increases linearly with concentration but aggregation can cause a saturation of absorbance at higher concentrations.[193, 194] Therefore, the absorbance of ZnTPP was measured over a range of concentrations, from 0.4 µM to 0.4 mM, with a 1 cm path length quartz cuvette and a Shimadzu UV-1800 spectrophotometer. A linear fit was then applied to each wavelength, after removing those where no light reached the detector, to extract the extinction coefficient. This is plotted in Fig.4.5, with the 95% error on the gradient denoted as a shaded area. The error is rather small, suggesting that a linear fit describes the data well and that it obeys the Beer-Lambert law up to 0.4 mM. For comparison, no evidence of aggregation described separately for clarity.
was observed up to 0.1 mM in THF.[180] Measurements with the laser setup used a cuvette with 0.2 mm path length and so higher concentrations were needed to achieve similar absorbances in the ideal range of 0.1 – 1 OD. However, these concentrations absorbed too much light across a 1 cm path length for their absorbance spectrum to be accurately measured.

All of the peaks in Fig.4.2 are observed, but since the B(0,0) peak is so much larger, those above 480 nm are shown scaled by a factor of 40. Peak positions, heights and their assignments based on comparisons to literature spectra are given in Table 4.1. There is a shoulder in the UV-Vis around 400 nm which likely corresponds to the B(1,0) transition, but it cannot be described quantitatively reliably. The minimum slit width on the spectrometer was 1 nm, which is too wide to fully distinguish between the B(1,0) and B(0,0) peaks. All peaks are within 5 nm of those observed by Yu et al. in Fig.4.2, where the differences may arise from slight miscalibrations between spectrometers. A small peak at 632 nm was also observed, which was tentatively assigned to the Q(0,1) transition as it is around 0.13 eV below the Q(0,0) peak. The sizes of the extinction coefficients vary greatly across the literature,[165] but those reported in Table 4.1 are all of the correct order of magnitude.

The MCD spectrum of ZnTPP in toluene was measured using the setup described in Chapter 2, and is plotted in Fig.4.6. A field of 0.4 T, a path length of 0.2 mm and a concentration of 1.3 mM were used. This solvent is higher than those tested in Fig.4.5 on account of the large difference in path difference. While no observations of ZnTPP aggregation in pure toluene could be found in the literature, aggregation cannot be
Figure 4.6: MCD spectrum of ZnTPP in toluene, measured using a 0.4 T field, 0.2 mm cuvette with a concentration of 1.3 mM at room temperature. Inset shows the Q(0,0) peak in the absorbance spectrum. The fits to the main panel and inset is given by Eqs.(4.1) and (4.2), respectively.
Table 4.2: Fitting parameters for the fits to the static MCD and the absorbance plotted in Fig.4.6.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Origin</th>
<th>$A_1$ /OD</th>
<th>$\sigma$ /eV</th>
<th>$E_0$ /eV (/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Q(0,0)</td>
<td>0.0275</td>
<td>0.033</td>
<td>2.09 (593)</td>
</tr>
<tr>
<td>2</td>
<td>Q(1,0)</td>
<td>0.144</td>
<td>0.039</td>
<td>2.26 (549)</td>
</tr>
<tr>
<td>3</td>
<td>(Solvent)</td>
<td>20.0</td>
<td>0.38</td>
<td>1.79 (693)</td>
</tr>
<tr>
<td>—</td>
<td>Q(0,0)</td>
<td>0.00674</td>
<td>0.0265</td>
<td>2.083 (595)</td>
</tr>
</tbody>
</table>

Since ZnTPP has no net spin, the ratio $A_1/D_0$ should give the magnetic moment for the excited $S_1$ state. The vibronic nature of the Q(1,0) transition means that this simple analysis only applies to the Q(0,0) peak.\[^{20, 173}\] The measured MCD spectrum is found to be well described by

$$MCD = 33 \times 10^3 \mu_B B \left[ A_1^1 \left( -\frac{\partial f^1(E)}{\partial E} \right) + A_1^2 \left( -\frac{\partial f^2(E)}{\partial E} \right) + A_0^3 f^2(E) \right]$$

(4.1)

where $f^i(E)$ is a normalised gaussian with width $\sigma^i$ centred on $E_0^i$ and $A$ is the amplitude of each term, as defined by Eq.(1.10). There are nine fitting parameters for this equation, with amplitude, width and centre fitted for each term. The prefactor comes from conversion from OD to mdeg and accounts for the field strength. Any prefactor which cancels with the prefactor in the $D_0$ term is neglected. The final term
is arbitrary and is only there to account for the solvent signal. The fit of Eq.(4.1) to the MCD spectrum is shown in Fig.4.6, where it clearly gives a good fit to the data, with only minor deviations. To calculate $D_0$, the function

$$A = D_0 f(E) + (bE + c)$$

was fit to the $Q(0,0)$ peak, where the second term accounts for the side of the $Q(1,0)$ peak. This is plotted inset to Fig.4.6, where it gives an acceptable fit to the data, but there has likely been some skewing of the fit due to the tail of the $Q(1,0)$ peak. The results of fits to both MCD and absorbance spectra are tabulated in Table 4.2. The centres of the $Q(1,0)$ and $Q(0,0)$ peaks are close to the those in absorption spectrum, which is likely due to the fit and also to slight wavelength calibration differences between spectrometers. For $Q(0,0)$, the widths of the MCD and absorbance peaks are close but not the same, which may make them less comparable. However, with these fits, one obtains that $\mu_z = 4.1 \mu_B$. Given the wide spread of magnetic moments across the literature ($1 - 5 \mu_B$ [24]), this is similar to the previously measured values of 2.48 and 3.52 $\mu_B$ in benzene and toluene, respectively.[172, 173] Given the fitting required and the difficulty in measuring completely accurate and comparable MCD and absorbance spectra, there can be considerable spread in $\mu_z$ determined by this method.

4.3 Transient Absorption

4.3.1 400 nm Photoexcitation

Transient absorption spectra were recorded for a 0.8 mM solution ZnTPP in toluene pumped with 400 nm, 350 $\mu$W (0.66 mJcm$^{-2}$) pulses with a 0.2 mm path length quartz cuvette. To prevent any photochemical degradation of the solution, and also because the $T_1$ lifetime is of a similar length to the repetition rate, the solution flowed through the cuvette for the duration of the measurement. This greatly reduced the chance of pumping or probing already photoexcited molecules; a clear drop in signal could be observed if the constant flow was stopped. Additionally, the cuvette was moved
The results of the TA are shown in Fig.4.7(a) as kinetic traces at selected wavelengths, and in Fig.6.4 as a 2D plot. The signal at all wavelengths increases greatly initially, dwarfing the XPM. Some wavelengths might show a fast initial rise in the first 100 fs, corresponding to VC in the $S_2$ state, but this is on a similar timescale to the XPM ($\sim 300$ fs long, see Fig.6.5) so it’s hard to be sure. After the initial photoexcitation there is a clear change within the first few picoseconds which manifests as a rise at some wavelengths and a fall at others. This most likely corresponds to the $S_2 \rightarrow S_1$ IC. The difference is most clearly seen between 507 and 552 nm, where the former is initially positive and then continues rising to 140 mOD in the first two ps. On the other hand, the latter is initially negative due to dominant GSB and then rises to 10 mOD on the
same timescale, reflecting an increase in ESA at 552 nm in $S_1$ relative to $S_2$. Once in the $S_1$ state there are slight changes from the VC within the state, but otherwise the signal is roughly constant for the next 100 ps. The second half of Fig.4.7(a) shows the signal at longer times, and there is a clear drop in the signal at almost all wavelengths over the 3 ns timescale. This clearly represents the $S_1 \rightarrow T_1$ intersystem crossing, and the accompanying reduction in ESA at most wavelengths. This is most clear for the trace at 552 nm, where the GSB is largest as this corresponds to the B(1,0) peak in the ground state absorbance spectrum. In contrast to all other wavelengths, 655 nm shows a growth on the $T_1$ timescale.

Difference spectra at selected time delays are plotted in Fig.4.7(b). There is a very large positive peak around 500 nm and a smaller, broader peak from 560–700 nm. There are three negative peaks at 552, 597 and 657 nm, but the latter two are smaller than the ESA so only appear as shoulders. The ground state absorbance spectrum in Fig.4.5 has two peaks within the wavelength region probed, at 552 and 594 nm. Since there are negative peaks in the TA at all time delays which also appear at 552 and 597 nm, these must be due to the GSB. However, there is no peak around 657 nm in the static absorbance spectrum, and curiously the peak seems to be most pronounced in the $S_1$ state, with no such peak present in the 0.2 ps spectrum. Features due to GSB must appear at all time delays and map to the static spectrum so this feature cannot be due to GSB. The feature could correspond to a lack of ESA from the $S_1$ at this wavelength, but the generally accepted interpretation is stimulated emission. The fluorescence spectrum shown in Fig.4.2 has two relevant peak at 596 and 645 nm that correspond to $S_1 \rightarrow S_0$ transitions. Although the probe pulse is weak, it can induce emission from the excited states which is observed as a net decrease in absorption with the same spectrum as the fluorescence. Therefore the peak at 645 nm, and some of the peak at 697 nm, is most likely due to stimulated emission. It is difficult to tell from the spectrum, given the overlapping emission, ESA and GSB, but there does not appear to be any shift in peak energies or large broadening or narrowing of peaks. The peak at 500 nm looks like it shifts from 500 nm to 507 nm and back, but this is likely due to a decrease in the ESA relative to the GSB.
Chapter 4.3.1

To ensure that evenly distributed absorption of single photons was the only way in which pump light was absorbed, the fluence dependence was measured. To do this, the TA spectra at 1.6 and 200 ps were recorded for several pump fluences and the TA at 510 and 600 nm plotted as a function of fluence. This is shown in Fig.4.8, where it is clearly linear up to 400 µW at which it begins to plateau. Applying a linear fit to the data below 400 µW shows that it is indeed linear and passes through the origin for all wavelengths and time delays. The cross section for two-photon absorption is expected to be rather large at 400 nm,[165, 195] yet as a two-photon process, one would expect this to depend on the square of the fluence, causing the TA to increase at higher powers. The excitation density typically saturates between 10 and 20% of excited molecules, so this is likely the cause of the saturation here.

The TA of the solvent was also measured, with the same pump power and fluence and in the same cuvette. To ensure that no ZnTPP remained in the cuvette, it was flushed through with toluene and methanol several times. No transient absorption signal was observed for pure methanol, besides the expected XPM around time-zero. However, when this methanol was replaced with the toluene used to dilute the sample,
Figure 4.9: Transient absorption of toluene pumped with 400 nm, 350 µW pulses at a range of time delays.

a 3 mOD TA signal could be measured. This has been plotted in Fig.4.9. The signal shows only a broad ESA across the wavelength range of the probe whose shape is roughly constant over time. However, its time-dependence is curious, showing a 2 ps decay then a 20 ps growth followed by a 1 ns decay back to 0 OD. Changing pump wavelength also produced similar spectra. The toluene used was uncoloured and had no visible impurities, yet no literature TA spectra for toluene could be found that showed a similar signal. This reproducible TA signal is a mystery but is most likely due to a dissolved contaminant. Given its small size in comparison to the ZnTPP TA, it should not have much effect on results but could skew some time constants. Repeating this measurement of the TA in purified toluene would be an ideal way to quantify its impact.

4.3.2 Global Fitting

To quantify the transient absorbance spectrum, a global, multi-exponential, fit was carried out using Eq.(3.2). The best fit to the data was achieved with 5 time constants: 0.1, 1.3, 10, 1200, > 30,000 ps and the fit to the data is plotted for selected wavelengths
in Fig.6.6. Here the shortest component represents a fit to both the VC in the $S_2$ state and the XPM. The 10ps component represents VC in the $S_1$ state.\[165\] Vibrational cooling typically causes blue-shift and narrowing of ESA features, although no such features are directly visible in the contour plot in Fig.6.4. Because of this, it cannot be modelled as a bilinear process, as the global fit assumes. However, its effect is typically small, especially in the case of the $S_1$ relaxation here. Therefore, a global fit with three components also gives an acceptable fit, resulting in time constants: $\tau_1 = 1.3$ ps, $\tau_2 = 1.2$ ns, $\tau_3 > 30$ ns. This fit is shown in Fig.6.7 and is clearly worse than the 5-exponential fit, as one would expect from a reduced number of fitting parameters, yet the main dynamics are described and it gives an adequate fit to the data. Furthermore, the three time constants found with the reduced fit are the same as those found by the 5-exponential fit, so the reduction in parameters does not impact the time constants. Since this assumes that the VC is negligible, the fit describes only bilinear processes. The $T_1$ lifetime is six orders of magnitude longer than that of the experiment so the time constant corresponding to its decay, $\tau_3$, is effectively infinite. It is assumed that $\tau_1$ corresponds approximately to the decay of $S_2$ and $\tau_2$ to the decay of $S_1$, since their values are similar to those in Fig.4.4. However, $\tau_2$ is significantly smaller than the value of 2 ns observed across the literature.\[177\] Longer time delays mean that the pump pulse travels further and therefore diverges more, resulting in a lower fluence at the sample at longer time delays. The pump width only changes by 8% at 400 nm between the ends of the translation stage, causing a 16% drop in fluence. Correcting $\tau_2$ to account for this only increase it to 1.3 ns, so this cannot be the cause of the discrepancy. If the unexpected solvent-only TA signal arose from a contaminant, then perhaps this quenches the ISC, making it happen faster than in a pure solvent. If the alignment of the pump beam changed slightly between 0 and 3 ns, then this would result in a smaller signal at longer times as the overlap worsens. This could also have contributed to making $\tau_2$ shorter than the literature.

The relaxation pathway proposed in Fig.4.4 clearly has many more than three time constants. Furthermore, the decay associated spectra given by the fit correspond, not to the spectra of the excited states, but instead to the component of the spectrum
which decays at a particular rate. Therefore, to convert the results of the fit into something closer to the pathway in Fig.4.4 further analysis is needed. To begin with, one can derive a set of coupled differential equations to model how the populations of the states change over time following photoexcitation. Letting the proportion of molecules in state $x$ be represented by $n_x$, the rate of change of the state, $\dot{n}_x$, is given by

\begin{align}
\dot{n}_{S_2} &= -(k_{IC,2} + k_{F,2}) \ n_{S_2} + P(t) \ n_{S_0} \\
\dot{n}_{S_1} &= k_{IC,2} \ n_{S_2} - (k_{ISC,1} + k_{F,1} + k_{IC,1}) \ n_{S_1} \\
\dot{n}_{T_1} &= k_{ISC,1} \ n_{S_1} - k_P \ n_{T_1} \\
\dot{n}_{S_0} &= k_{F,2} \ n_{S_2} + (k_{F,1} + k_{IC,1}) \ n_{S_1} + k_P \ n_{T_1} - P(t) \ n_{S_0} 
\end{align}

(4.3)

for each of the relevant states. Removing vibrational cooling components to the multi-exponential global fit described previously had minimal impact on the time constants. Therefore, VC is not included in Eq.(4.3), making the assumption that its effect can be ignored. To aid readability, instead of time constants, rate constants $k_i = \tau_i^{-1}$ with the same subscript as the corresponding time constant are used. The pump is assumed to only excite the $S_0 \rightarrow S_2$ transition and its action is represented by $P(t)$. Given that the $T_1 \rightarrow S_0$ relaxation is orders of magnitude longer than the experimental timescale, an infinite relaxation time is assumed in Eq.(4.3). To simplify the analysis, $P(t)$ is assumed to be an instantaneous impulse (a Dirac delta function) and only $t > 0$ are considered. Excluding $P(t)$, Eq.(4.3) is a linear function of the populations and can be rewritten in a more easily solveable matrix form. This changes the equation to
\[ \dot{n} = K n, \] where \( n = (n_{S_2}, n_{S_1}, n_{T_1}, n_{S_0}) \) and \( K \) is a 4x4 matrix, given by

\[
K = \begin{pmatrix}
-(k_{IC,2} + k_{F,2}) & 0 & 0 & 0 \\
-k_1 & -&(k_{ISC,1} + k_{F,1} + k_{IC,1}) & 0 & 0 \\
0 & k_{1T} & 0 & 0 \\
k_{F_2} & 0 & (k_{F,1} + k_{IC,1}) & 0 & 0 \\
(-k_1) & 0 & 0 & 0 \\
\varphi_{21} k_1 & -k_2 & 0 & 0 \\
0 & \varphi_{1T} k_2 & 0 & 0 \\
(1 - \varphi_{21}) k_{20} & (1 - \varphi_{1T}) k_{10} & 0 & 0
\end{pmatrix}
\] (4.4)

Since Eq.(4.3) is linear, the solution of \( \dot{n} = Kn \) is a linear combination of exponential decays, whose rate constants are the eigenvalues of \( K \). These will simply be its diagonal values since \( K \) is a triangular matrix. Letting \( k_1 = (k_{IC,2} + k_{F,2}) \) and \( k_2 = k_{ISC,1} + k_{F,1} + k_{IC,1} \), there are three unique eigenvalues \(-k_1, -k_2 \) and 0 which correspond directly to the time constants produced by the global fit. The remaining values in the matrix can then be written in terms of the branching ratios \( \varphi_{21} \) and \( \varphi_{1T} \). The model does not therefore distinguish between \( k_{F,1} \) and \( k_{IC,1} \), since both will give the same contribution to the TA spectrum of a transfer of population from \( S_1 \) to \( S_0 \).

At \( t = 0 \) the state populations are assumed to be \( n(t = 0) = (N, 0, 0, 1 - N) \), where \( N \) electrons have been excited instantaneously from \( S_0 \) to \( S_2 \) by the pump pulse. Using
Figure 4.10: Relative occupancies of each state as a function of time, calculated using Eq. (4.5) with $N = 0.12$, $k_1 = (1.3 \text{ ps}^{-1})$, $k_2 = (1.2 \text{ ns}^{-1})$, $\varphi_{21} = 1$, $\varphi_{1T} = 0.87$. To make the plot clearer, $1 - n_{S_0}$ is plotted rather than $n_{S_0}$.

As a check for this, at $t \rightarrow +\infty$ all molecules should be in $T_1$ or $S_0$, and at all times, the sum over all $n$ should equal one; both of these are found to be true. The populations of each state over time are plotted in Fig. (4.5) where 12% of the molecules enter $S_2$ initially before relaxing into $S_1$. They then relax from $S_1$ into $S_0$ and $T_0$ over much longer timescales.

The total TA spectrum, $D(\lambda, t)$ is constructed from the decay associated spectra,
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\[ D_1, D_2, D_3 \text{ and corresponding exponential as} \]

\[
D(\lambda, t) = D_1 e^{-k_1 t} + D_2 e^{-k_2 t} + D_3 \\
= D_s n_s + (D_s - \gamma D_F)n_s + D_{T_1}n_{T_1} - D_{S_0}(1 - n_{S_0}) 
\]

Likewise, \( D(\lambda, t) \) can also be written as a sum of the transient population of each state multiplied by their contribution to the spectrum. The species associated spectrum (SAS) for state \( x \) is labelled \( D_x \). This is the spectrum which would be observed if all molecules were in state \( x \). Stimulated emission from the \( S_1 \) state is observed in the TA spectrum, which should follow the shape of fluorescence spectrum, \( D_F \). The intensity of the probe pulse is sufficiently weak that the stimulated emission will have a negligible effect on the population of the \( S_1 \) state, but the size of the effect on the TA is unknown. Therefore the contribution to the TA from \( S_1 \) is given as \( D_{S_1} - \gamma D_F \), where \( \gamma \) is a parameter to account for the size of the stimulated emission spectrum. The final term in Eq.(4.6) is negative to account for the ground state bleach.

Since the DAS correspond to different functions in time (i.e. two to exponentials and one to a constant), by expanding Eq.(4.6) using the expressions in Eq.(4.5) and collecting like terms, one can derive expressions for the SAS in terms of known spectra.

\[
D_{S_2} = \frac{1}{N} (D_1 + D_2 + D_3) + \left( \varphi_{21} \varphi_{1T} - 1 \right) + \varphi_{21} \frac{k_1 - \varphi_{1T} k_2}{k_1 - k_2} D_{S_0} + \alpha \gamma \frac{k_1}{k_1 - k_2} D_F \\
D_{S_1} = \frac{1}{\varphi_{21} N} \left( D_3 + \frac{k_1 - k_2}{k_1} D_2 \right) + \varphi_{1T} D_{S_0} + \gamma D_F \\
D_{T_1} = \frac{1}{\varphi_{21} \varphi_{1T} N} D_3 + D_{S_0} 
\]

The branching ratios \( \varphi_{21} \) and \( \varphi_{1T} \) correspond to the quantum yields of \( S_2 \rightarrow S_1 \) IC and \( S_1 \rightarrow T_1 \) ISC, respectively. From the literature values for fluorescence lifetimes in Fig.4.4 they therefore have values of 1 and 0.87, respectively. The size of the stimulated emission, \( \gamma \), is unknown and must be estimated from the resulting SAS as the value
that best removes the peak at 650 nm. Since the fluorescence spectrum, and therefore $D_F$, is in arbitrary units, the absolute value of $\gamma$ is arbitrary.

The initial fraction of photoexcited molecules, $N$, can be estimated from the experimental parameters. From the Beer-Lambert law, the fraction of absorbed photons is given by $1 - 10^{-A}$, where $A$ is the absorbance. The number of photons per unit area of a pulse is given by the fluence, $F$, divided by number of photons per unit energy. Therefore, the number of photons absorbed per unit area is given by

$$N_{\text{abs}} = \frac{(1 - 10^{-A})F\lambda}{hc_l}$$

(4.8)

where $h$ is Planck’s constant and $c_l$ is the speed of light. Approximating the laser as exciting an area of radius $r$ at the focus, then an estimated $N_{\text{abs}}\pi r^2$ photons are absorbed. The volume illuminated by the laser is therefore $l\pi r^2$, where $l$ is the path length. The number of molecules in this volume is given by $N_V = N_A cl\pi r^2$, where $N_A$ is the Avogadro constant and $c$ is the concentration. Assuming that one molecule absorbs either zero or one photon(s), the fraction of excited molecules, $\kappa$, is given by

$$\kappa \approx \frac{(1 - 10^{-\epsilon cl})F\lambda}{hc_l N_A cl}$$

(4.9)

where the absorbance has been replaced with $A = \epsilon cl$. For these measurements, $c = 0.8$ mM, $l = 0.02$ cm, $\epsilon = 2 \times 10^4$ M$^{-1}$cm$^{-1}$, $\lambda = 400$ nm and $F = 0.6$ mJcm$^{-2}$. Substituting these into Eq.(4.9) gives $\kappa \approx 8\%$. This is of course an approximation, as molecules may absorb more than one photon and the profile of the laser beam is not a perfect, homogenous circle. Furthermore, it does not take into account that the molecules at the front will be subject to a much higher photon density than those at the back. However, it gives a reasonable estimate as to the order of magnitude of $N$.

To remove the GSB peak at 550 nm in the SAS, the spectrum measured in Fig.4.5 was used as $D_{S_0}$ with $N = 12\%$, which is close to the 8\% predicted by the back of the envelope calculation above. It was assumed that $N$ should be as small as possible while ensuring that all SAS are positive, resulting in $N = 0.12$. To remove the SE peak at 650 nm, as well as the remainder of the peak near 600nm, as best as possible,
the fluorescence spectrum measured by Yu et al. in Fig.4.2 was subtracted using \( \gamma = 1.8 \times 10^{-4} \). Since this fluorescence spectrum was measured in benzene, and to account of any differences in wavelength calibration, the spectrum was also red-shifted by 10 nm to best remove the peaks from the SAS. There is significant error on \( \gamma \) since the removal of the SE was judged by eye. The resulting SAS spectra, as well as the fluorescence and absorbance spectra, are plotted in Fig.4.11.

As a check for the fit, the SAS were substituted back into Eq.(4.6). This reconstructed TA spectrum is plotted against the measured TA in Fig.4.12 at several time delays. It clearly provides a good fit to the data at the time delays considered, with only minor deviations around 600 and 650 nm.

All three SAS have similar shapes, with a large peak around 500 nm and a very broad peak around 600 nm. The \( S_1 \) state has the greatest absorbance, and the \( T_1 \) the lowest. As was clear from the original TA spectrum, the \( S_1 \) state has non-zero absorbance at 550 nm. A broad absorption band is observed for \( S_2 \) from 570 nm onwards, but the peaks here around 600 and 650 nm likely result from the subtraction
Figure 4.12: Reconstructed fit to TA from Eq.(4.6). Fit shown as solid black lines and the difference spectra at different times are plotted as dotted lines. The fit almost exactly follows the difference spectra.

of the GSB and SE. Given the simplistic analysis presented here, which assumes monoeXponential decays and neglects vibration cooling, the SAS are likely not a perfect absorbance spectrum for the excited states. However, while TA for ZnTPP have been reported previously, and the time constants found from these used to inform Fig.4.4, the absorbance spectra of the excited states have not. Rodriguez et al. measured the TA and estimated an $S_1$ extinction coefficient of $5 \times 10^4$ M$^{-1}$cm$^{-1}$ at 460 nm. The peak absorbance at 520 nm for the $S_1$ state by my analysis is $7.5 \times 10^4$ M$^{-1}$cm$^{-1}$, which is of the same order of magnitude. Similar analysis was carried out on met-myoglobin, which contains an iron porphyrin, to extract the SAS and the resulting spectra were quite similar to each other, suggesting that excited state spectra in porphyrins may have similar structures to one another.[196] They observed a peak in TA between 400-500 nm and a broad, unstructured spectrum at redder wavelengths. The authors note that this structure is observed in many other free-base or metalloporphyrins. Calculations of the excited state structure of ZnTPP typically find that the states above and below the LUMO and HOMO, respectively are relatively closely spaced compared
Figure 4.13: TA spectra measured using 400 and 420 nm pump pulses at 200 ps. Inset is the TA signal at 200 ps for two wavelengths as a function of pump power. A clear non-linearity is observed.

to the HOMO-LUMO gap.[168] A large number of overlapping bands would cause a relatively featureless absorbance spectrum, as observed in Fig.4.12. Removal of the SE and GSB both relied on assumptions as to the shape of the SAS and so introduced significant error. The minimal absorbance at 550 nm is likely due to inadequate removal of the GSB, yet using a larger value of $N$ instead adds large positive peaks around 600 and 650 nm, like the ones seen in the $S_2$ SAS. Without any additional points of reference for optimising the spectra, these SAS can only be speculative. Since the fluorescence spectrum was taken from the literature and in benzene, it may be slightly different for this solution, introducing another large source of error.

4.3.3 420 nm Photoexcitation

The absorbance of ZnTPP at 420 nm is clearly much greater than at 400 nm. Therefore with the hope that this could increase signal-to-noise, the TA and TRMCD were recorded at a concentration of 1.3 mM using 420 nm pump light with a power of 500 µW — parameters were otherwise the same. Due to time constraints, the TRMCD could
not be repeated in full with a 400 nm pump, so measurements are presented at both 400 and 420 nm. A comparison of the TA spectra at 200 ps is plotted in Fig.4.13. The 420 nm pump TA shows much higher signal at bluer wavelengths, and slightly lower at redder wavelengths. Since the absorbance at the pump wavelength is very large, all of the pump pulse is absorbed and there is negligible pump scatter. However, the large absorbance means that the pump pulse is absorbed at the start of the cuvette, creating a very sharp gradient of photoexcited molecules. The TA signal at 200 ps plotted inset to Fig.4.13 shows a clear non-linear dependence on power, likely due to this very inhomogenous excitation. Measurements at lower fluences find that the power dependence is still non-linear below 200 µW, a region which appears linear in Fig.4.13. A similar non-linearity was observed in the fluence dependence at 400 nm, yet here the measurement extends further into the non-linear regime where the signal begins to decrease with fluence.

TA spectra were measured at several time-delays at 420 nm. Applying an exponential fit to the trace at 600 nm gave $\tau_2 \sim 1.5$ ns, where only six time-delays were measured so this is not a very reliable fit. It is larger than the value obtained by the 400 nm pump TA but this is still smaller than the expected value of 2 ns.

### 4.4 Time-Resolved Magnetic Circular Dichroism

#### 4.4.1 420 nm Photoexcitation

Given that ZnTPP has a strong static MCD spectrum, time-resolved MCD spectra were measured simultaneously to the TA spectra above, while applying a 0.4 T field. ZnTPP is diamagnetic rather than ferromagnetic, so while its static MCD spectrum is large for such materials, it is small compared to a ferromagnet like CGT. If the size of the GSB in the TA corresponds to photoexciting $\sim 10\%$ of the molecules, then there will be a similar GSB in the MCD on the order of 2 mdeg. This is significantly smaller than the TRMCD from CGT and is close to the sensitivity of the setup. Therefore, to achieve a useful TRMCD spectrum, each spectrum at a given time-delay was averaged over at least $3 \times 10^5$ shots, rather than the usual $\sim 10^3$. This pushed the noise level
Figure 4.14: TRMCD spectra of ZnTPP in toluene at various times following photoexcitation with 420 nm pump. The static MCD spectrum, scaled by $-1/23$ is also plotted to show the shape of the contribution from ground state bleach. Much of the spectrum appears to follow the static MCD, except for a large peak around 600 nm. Inset is the TRMCD at 600 nm plotted as a function of time, along with an accompanying fit.
in the spectrum down to < 0.1 mdeg, enabling changes in small TRMCD signals to be captured. This also simultaneously records the corresponding TA spectrum. However, a major limitation of this method of acquisition is that it takes a long time to acquire a spectrum at a given time-delay (≈ 30 minutes). Therefore, measurements at shorter times where chirp correction is required are unfeasible. This makes it difficult to access the $S_2$ state, which is fully depopulated after a few ps.

TRMCD spectra at several time-delays are plotted in Fig.4.14, where they were measured with 420 nm, 500 µW pump at a concentration of 1.3 mM. The TRMCD at -100 ps is clearly just noise, reflecting the lack of pump scatter in the data, which may show small, field-dependent scattering if it were present. There is a lot of the noise in the data, since the signal is so small, so only large trends in the time-dependence of the signal are discernible. Since GSB is expected to be present in the spectrum, the static MCD spectrum is also plotted in Fig.4.14, scaled by $-1/23$ to best match the data. The TRMCD does appear to follow the static MCD spectrum, especially the $A_0$ term around 550 nm and this GSB signal has no clear time-dependence, as one would expect with such a long $T_1 \rightarrow S_0$ relaxation. Below 530 nm, there appears to be some TRMCD signal but this is caused by fluctuations in the white light and cannot reliably be repeated. The most clear feature is a peak at 600 nm which increases over time, and to the blue side of this there is a sharp peak which shows no clear time-dependence. This latter peak could be a particularly noisy wavelength in the probe spectrum, but there is a reproducible and time-dependent structure to the 600 nm peak. Inset to Fig.4.14 is the signal at 600 nm plotted as a function of time. Excluding the solvent MCD, the GSB contribution at 600 nm is around +0.14 mdeg. Therefore, the TRMCD at 600 nm was found to be well described by $2.0e^{-t/1500} + 0.14$ and this fit is plotted alongside the data in Fig.4.14. Given the long phosphorescence, the recovery of the ground state over the timescale of the experiment is negligible, thus it is accounted for by a constant term in this exponential decay. This 1.5 ns decay is identical to the $\tau_2$ measured for the TA following 420 nm pump, suggesting that the feature arises from the $S_1$ state. However, while the data presented in Fig.4.14 is compelling, Fig.4.13 shows that the pump fluence is firmly in the non-linear regime.
Figure 4.15: TRMCD spectra 200 ps following 400 nm photoexcitation for different initial field directions. The negative field spectrum has been inverted to best show the overlap and the 68% confidence intervals are also plotted.

4.4.2 400 nm Photoexcitation

From Fig.4.8, the 400 nm TA is linear in the pump power up to 400 µW, unlike with 420 nm pump. Therefore the TRMCD measurements were also carried out for the 350 µW, 400 nm pump pulses at a concentration of 0.8 mM. Since the TRMCD is measured by subtracting consecutive TA spectra recorded under opposing fields from one another, if the TA changes slowly over time, then this change may be measured as an erroneous TRMCD. For example, if the flow of the sample through the cuvette were to stop, then the TA signal would slowly decrease over time. To avoid this, one can reverse the order of the applied magnetic fields (e.g. -++-... instead of +--+....) when measuring the TRMCD. This will reverse the sign of the measured TRMCD signal, but the long-term change in the TA will be unaffected. TRMCD spectra at 200 ps are plotted in Fig.4.15 for opposite initial field directions. To best compare the two, the negative field spectrum is inverted and the 68% confidence intervals are plotted. The spectra clearly overlap very well with one another across most of the spectrum. The only exception to this is below ∼530 nm, where the noise increases dramatically due to
fluctuations in the white-light spectrum. TRMCD signals at the shortest wavelengths are therefore unreliable. However, the rest of the spectrum is well reproduced, with an $A_1$ term from the GSB visible around 560 nm, and the previously observed peak near 600 nm. The exact heights of the peaks, especially those in the GSB, are subject to high levels of noise but even the confidence intervals preserve the structure. The structure is clearly reproducible and not an artefact of the high absorbed fluence at 420 nm, nor due to a slowly-varying TA spectrum. Additionally, while a small TA signal could be observed at 200 ps from the solvent, solvent only measurements were found to show no measurable TRMCD. It should however be noted that Fig.4.15 is quite different to Fig.4.14, even if the major features are still present at the same features, which could be a result of the very different absorbed pump fluence. The data in the former is also less noisy, which is likely due to a greater amount of probe light passing through the sample due to the lower concentration, although could also be due to a better optimised supercontinuum.

Figure 4.16: Schematic of proposed schemes for "$C_0$" terms in transient spectra. (a) Photoexcitation from a populated state to a higher-lying state. (b) Stimulated emission from an excited state.
4.4.3 Discussion

While the GSB (the bleached steady-state MCD spectrum) can be identified through comparison to the TRMCD, the identity of the 600 nm peak is unknown. There is a peak in the static MCD at 600 nm, but this is part of an $A_1$ term centred on the $Q(0,0)$ transition. In contrast, the 600 nm peak in the TRMCD is broader, has no negative counterpart and decays at the same rate as the $S_1$ state. Because of this time-dependence, it is most likely due to the $S_1$ state. As shown by the $A_1$ terms in the static spectrum, the $S_1$ state is degenerate and this degeneracy is lifted when a field is applied. Once the photoexcited population has undergone internal conversion and vibrational cooling into the bottom of $S_1$ state, there will be a larger population in the lower-energy sublevel. Such a population difference in an excited state could contribute to the TRMCD through either $S_1 \rightarrow S_n$ absorption or $S_1 \rightarrow S_0$ stimulated emission. These scenarios are depicted in Fig. 4.16(a) and (b), respectively.

If the $S_1$ state were the ground state of a paramagnetic molecule, then a population difference between sublevels in the state would cause a $C_0$ term at the $S_1 \rightarrow S_n$ transition. In the method used here, the field is reversed rather than the probe helicity and reversing the sign of the field reverses the order of the sublevels. Left-handed circularly polarised photons, $\sigma^+$, have a positive angular momentum and so, to conserve angular momentum, when absorbed they can only cause transitions where $M_J$ increases. Therefore, if $S_n$ is assumed to be nondegenerate with $M_J = 0$ then only the transitions from the $S_1$ sublevel with negative $M_J$ need to be considered. Since the $A_1$ term in the static MCD spectrum is positive, it can be assumed that the sublevel with the most negative value of the $M_J$ quantum number will be lowest in energy when a positive field is applied. Therefore, after photoexcitation, this sublevel will have a larger population under a positive field compared to a negative one. The TRMCD is calculated by subtracting the absorbance under a positive field from a negative field, so the $C_0$ term resulting from $S_1 \rightarrow S_n$ absorption will be positive.

Stimulated emission is observed in the TA spectrum around 600 nm. Given the width and noise of the peak in the TRMCD, it is difficult to tell where the exact peak position lies but it clearly overlaps somewhat with the 600 nm peak in the fluorescence
and TA. This SE corresponds to the $S_1 \rightarrow S_0$ transition. For each incoming $\sigma^+$ photon of the probe, two $\sigma^+$ photons will be emitted. Therefore, to conserve angular momentum, the SE can only correspond to transitions with a decrease in $M_J$. $S_0$ has $M_J = 0$ so only the $S_1$ sublevel with $M_J > 0$ needs to be considered. After photoexcitation, this sublevel will have a smaller population under a positive field compared to a negative one. This is the opposite situation to Fig. 4.16(a), and as such will result in a negative $C_0$ term. Given that the GSB contribution to the TRMCD has the same shape as the inverted static MCD spectrum, the 600 nm peak in the TRMCD is positive. Therefore the peak is most likely due to $S_1 \rightarrow S_n$ absorption rather than $S_1 \rightarrow S_0$ stimulated emission.

As can be seen in Fig. 4.16, a $C_0$ term has a non-derivative shape even though both $A_1$ and $C_0$ terms both arise from the splitting of sublevels. The MCD spectrum from a $C_0$ without a population difference will have a derivative-like shape. However, the population difference typically makes the smaller peak negligible. In the two cases presented in Fig. 4.16, the main peak of the $C_0$ term has an adjoining, smaller peak of opposite sign. For Fig. 4.16(a), the smaller peak lies at longer wavelengths (lower energies) whereas for Fig. 4.16(b), the opposite occurs. Since the two methods give rise to different shapes, it is worth estimating the size difference between the two peaks. Assuming that there are two sublevels in the $S_1$ state which are shifted by $\pm \mu_z B$, the relative population of each state can be calculated as

$$ P(\pm) = \frac{e^{\pm \beta}}{e^{+\beta} + e^{-\beta}} \approx \frac{1}{2} (1 \pm \beta) \quad (4.10) $$

where $\beta = \frac{\mu_z B}{k_B T}$. If transitions from both states to $S_n$ have the lineshape $f(E)$, similar to Eq. (4.1), then the resulting MCD signal can be written as

$$ \Delta A = \frac{1}{2} (1 + \beta) f(E + \mu_z B) - \frac{1}{2} (1 - \beta) f(E - \mu_z B) \quad (4.11) $$

This can be calculated using the experimental parameters $B = 0.4$ T, and $T = 295$ K, along with the fitting parameters from Table 4.2, $\mu_z \approx 4$ and $\sigma \approx 0.03$ eV. Upon plotting this, one finds that the ratio of the positive and negative peaks is around 70,
which is clearly smaller than the noise for a positive peak of $\sim 2$ mdeg. Therefore the side peak cannot be used to discern between the two mechanisms here.

The stimulated emission contribution to the TA appears to follow the fluorescence spectrum with a strong peak at 650 nm and a weaker peak at 600 nm. Therefore one would expect that the MCD signal from this fluorescence spectrum would also have a similar shape, with two $C_0$ terms centred on the Q(0,0) and Q(0,1) transitions. However, while there appears to be a shoulder at 650 nm in the TRMCD, it is much smaller than the 600 nm peak. This provides further evidence that SE is not the cause of the TRMCD peak.

$A_{C_0}$ term in a MCD spectrum usually corresponds to a peak in the absorbance spectrum. However, upon comparing the TRMCD to the $S_1$ SAS, there are no such features around 600 nm. If the SAS is relatively featureless due to there being many $S_1 \rightarrow S_n$ transitions whose peaks overlap, then there should many overlapping peaks in the TRMCD as well. This is clearly not the case. The SAS are unreliable given the assumptions required to derive them, however no peak is observed at 600 nm in the TA spectrum to begin with. It could therefore be the case that these were invalid and there is in fact a peak at 600 nm in the TRMCD. Yet this does not account for the remaining broad absorption feature which must show some MCD activity given that the $S_1$ state itself is degenerate. Since the $S_1$ state is a singlet, then it should be possible to calculate $\mu_z$ for the $S_1$ state using the absorbance and TRMCD, if the feature is due to $S_1 \rightarrow S_n$ transitions. The dipole strength in OD is the value of the SAS at 600 nm multiplied by the fraction of molecules in the $S_1$ state at 200 ps. Unlike with the $A_{C_0}$ term in the static spectrum, the lineshape cancels so the peak value can be used instead. This results in $D_0 = D_{S_1}(600 \text{ nm})n_{S_1}(200 \text{ ps}) \sim 0.4 \times 0.12 = 0.05$ OD. By comparison to Eq.(1.10), the size of the $C_0$ term is given by

$$C_0 = \frac{TRMCD(600 \text{ nm, 200 ps})[\text{mdeg}]}{33 \times 10^{-3}} \frac{k_B T}{B} = \frac{2.7}{33 \times 10^{-3}} \frac{k_B \times 295}{0.4} = 0.090 \mu_B$$

(4.12)

where the factor of $33 \times 10^3$ comes from converting from mdeg to OD. Since the SAS were found from the 400 nm pump measurements, the size of the TRMCD at 600 nm and 200 ps from Fig.4.15 is used. Therefore, the magnetic moment of the $S_1$ state is
Discussion

found to be

\[ \mu_z = \frac{C_0}{D_0} = 1.8 \mu_B \]  

(4.13)

which is roughly half the value found from analysis of the static MCD spectrum. This estimate for \( \mu_z \) will not be valid for stimulated emission, since the absorption and SE cross sections are not equal.

A \( B_0 \) term could also cause the signal. These are typically small, but there is already significant mixing of states in ZnTPP without the field as well as evidence of small \( B_0 \) terms in the static MCD spectrum.[173] Calculations predict many states close together in energy above the LUMO so field-induced mixing of the \( S_n \) state could cause the peak at 600 nm. However, if a large number of states are present then they should all produce \( B_0 \) terms, yet only one such peak is observed. \( B_0 \) terms are typically identified by ruling out \( A_1 \) or \( C_0 \) terms. They are also the hardest to identify computationally, requiring the sum over all states.

Measuring TRMCD at low temperatures and high fields would help to identify the states involved. Only \( C_0 \) terms are temperature dependence so if the height of the TRMCD peak changes at 1/\( k_B T \), then it is clearly a \( C_0 \) term. Furthermore, at lower temperature, new \( C_0 \) terms may become visible, allowing for more states to be identified. A stronger magnetic field would increase the size of the (TR)MCD spectrum, and improve the signal to noise. Additionally, at the highest fields and lowest temperatures, \( C_0 \) terms saturate as the low-energy sublevel becomes filled, providing another way to identify the peak and measure \( g \) factors. Suspension of the molecule in an optical glass or polymer film such as PMMA could allow for low temperature measurements with our current experimental setup. Magnetic field strength is limited to 0.4 T by our current magnet, but a superconducting magnet would allow for optical measurements at field strengths an order of magnitude larger than this.

Peaks from \( S_1 \rightarrow S_n \) and \( T_1 \rightarrow T_n \) transitions appears in the near IR.[178, 191] This range could not be measured here due to the poor supercontinuum intensity in this region. Given that there are peaks in the ESA, these are good candidates for further TRMCD measurements, and could give more reliable measurements of \( \mu_Z(S_1) \) and \( \mu_z(T_1) \).
The most straightforward improvement is simply more measurements. The TRMCD spectra shown above took a long time to acquire until a reliable signal was observed. However, a greater time resolution and a better sensitivity would allow for much more confident quantitative analysis. Furthermore, acquisition of spectra at short times would enable measurement of the TRMCD spectrum for the $S_2$ state, which is short-lived enough to require chirp correction. This spectrum would show the same GSB features, with a peak at 600 nm that grows as the $S_1$ state is populated, and also potentially new features corresponding to $S_2 \rightarrow S_n$ transitions.

4.5 Conclusion

The overall conclusion for the above studies on ZnTPP in toluene is that a MCD spectrum of the transiently populated $S_1$ state has been measured. Static absorbance and MCD spectra characterised the solution and provided reference spectra for analysis of the transient spectra. Additionally, a value for the $S_1$ magnetic moment of $4.1 \mu_B$ was calculated. Transient absorbance of the solution following photoexcitation of the B(1,0) transition was measured and found to show overlapping ground state bleach, excited state absorption and stimulated emission features. Therefore, a global fit was applied in conjunction with a kinetic model to extract the absorbance spectrum associated with each excited state. However, this analysis assumed that vibrational cooling was negligible and made many further assumptions as to the shape and size of the SE and GSB. Given that the resulting SAS had a large dip at the main GSB features, the SAS are likely inaccurate and the aforementioned assumptions possibly invalid. Time-resolved MCD spectra were measured at several time-delays following photoexcitation. Comparison of this to the static MCD spectrum revealed that a portion of this signal was due to a MCD "ground state bleach", yet a large peak centred on 600 nm was unaccounted for. This peak decayed with the $S_1$ population and the value for the $S_1$ magnetic moment it predicted did not match with that calculated from the static MCD spectrum. This likely arises from a transient $C_0$ term due to a $S_1 \rightarrow S_n$ transition. However, it could also arise from a $B_0$ term. Variable temperature and field measurements,
as well as those with a higher wavelength range, are required to confidently assign this feature. Furthermore, static absorbance measurements at higher concentrations are needed to rule out the effects of aggregation at the high concentrations used.
Chapter 5

Summary and Outlook

This thesis outlined the development, implementation and testing of a broadband, ultrafast polarisation and absorbance spectrometer and its subsequent application to several different test systems. Following this, more detailed and in-depth studies of two further systems with the spectrometer were described.

To develop the spectrometer described in chapter 2, a theoretical framework using Jones calculus was used. From this, analytical expressions for the signal measured with both broadband (CCDs) and monochromatic (PDs) methods were found. These acted as theoretical proof of concept, and were also extended to include the impact of imperfect optics on the signal. The setup was built from an existing broadband TA spectrometer. Its broadband capabilities were tested on glass and CoCl$_2$ solutions and found to agree well with literature in the static case. Transient measurements were carried out on a Ni film to confirm that both transient changes to ellipticity and rotation can be measured across a wide spectral range. The sensitivity of this setup could be improved for many samples by using a stronger magnet. Using cameras which can function at higher repetition rates or statistical analysis of data during acquisition could also help improve signal-to-noise. The former would allow for much faster acquisition, which was observed to improve sensitivity dramatically for the photodiodes. The latter would require no new equipment and could make acquisition more efficient by taking into account the spectrally correlated noise.

The first major study using this spectrometer was on the layered ferromagnet CGT.
Time-resolved magneto-optics had previously been measured for this material, yet only using single wavelengths. Using the broadband approach, I demonstrated that it had a non-trivial TRMCD spectrum and that measurement of polarisation change at a single wavelength is not enough to determine the demagnetisation. Type II demagnetisation dynamics were observed, matching previous observations and similar to the predicted ellipticity spectrum. Also observed was a contribution from photoexcited electrons which corresponded to $(5p - e_g)\sigma^* \rightarrow t_{2g}^\downarrow, e_g^\downarrow$ transitions. Measurements at different temperatures showed that this contribution persisted above $T_C$ yet the demagnetisation did not. Fast decay in the TT had the same time constant as the photoexcited electrons so likely arose from the same mechanism, yet a slow growth in the TT could not be confidently assigned. Measurements over a wide range of temperatures and powers with a finer resolution than presented here could help assign these features by investigating their dependence on the saturation magnetisation and the number of photoexcited carriers. Demagnetisation could be more confidently assigned by using a transverse rather than longitudinal field to observe ferromagnetic resonance or by measuring the time-dependent change in the hysteresis loop. An extension could also be to try pumping above and below the band gap of CGT with the idler output of the NOPA to observe the dependence of the demagnetisation dynamics on photoexcited carrier density. Measurements on a greater set of samples would also of course provide more compelling results, and would allow for studies of the dependence of transient properties on the thickness.

TRMCD spectra were measured for ZnTPP at a range of time delays. To my knowledge, broadband magneto-optic spectra have not previously been measured for a molecular system on picosecond timescales before so this demonstrates a novel method through which to further study electronic structure in inorganic systems. To understand this spectrum, static absorption and MCD, as well as TA were also measured. Fits to the Q(0,0) term in both static spectra found a magnetic moment of $4\mu_B$, which lies within the wide range of literature values. The TRMCD spectrum showed a ground state bleach contribution with the same shape as the inverted static MCD spectrum and strong peak around 600 nm, which decayed on the same timescale as the $S_1$ state.
Careful consideration of the $C_0$ terms expected from $S_1 \rightarrow S_n$ ESA or $S_1 \rightarrow S_0$ SE found that this peak likely arises from an $S_1 \rightarrow S_n$ transition. By fitting a kinetic model to the TA spectrum to extract the absorbance of the $S_1$ state, a magnetic moment of 1.8 $\mu_B$ was obtained for the $S_1$ state. This is still within the range of the literature values, but is clearly different to the value found from the static spectrum. A transient $B_0$ term could give a similarly shaped feature so temperature dependent measurements would help to elucidate this further. Measurements across a wavelength range which extends further into the near IR could investigate promising peaks in the TA which may be MCD active in the $T_1$ and $S_1$ states. Finally, a greater time-resolution in the first few picoseconds could allow for measurement of the MCD spectrum of the $S_2$ state. It is hoped that these measurements open the way for further utilisation of ultrafast, broadband magneto-optics for investigating electronic structure in excited states in a wide range of materials.
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Chapter 6

Appendix

Several figures which complement the main text of the thesis are presented here in the appendix.
Figure 6.1: TRMCD with 800nm pump pulses for sample A. (a,c,e) Contour plots at a fluence of 1.0 mJcm$^{-2}$ at 42 K, 61 K and 82 K, respectively. (b,d) Kinetic traces at a fluence of 1.0 mJcm$^{-2}$ at 42 K and 61 K, together with the global fit to the data. 82K could not be fit. (f,g) Contour plots at 20 K with fluences of 0.2 and 0.5 mJcm$^{-2}$. 
Figure 6.2: Transient transmittance with 1.0 mJcm\(^{-2}\), 800nm pump pulses for sample A. (a,c,e) Contour plots showing the raw data as a function of both probe wavelength and time delay. (b,d,f) Kinetic traces showing the global fit to the data at selected probe energies. Data recorded at three temperatures: (a,b) 42 K, (c,d) 61 K, (e,f) 82 K.
Figure 6.3: Transient transmittance at 20 K with 800 nm pump pulses for sample A. (a,c) Contour plots show the raw data as a function of both probe wavelength and time delay. (b,d) Kinetic traces at selected probe wavelengths showing the global fit to the data. Data recorded using fluences of (a,b) 0.2 mJcm\(^{-2}\) and (c,d) 0.5 mJcm\(^{-2}\).
Figure 6.4: Contour plot showing the transient absorbance of 0.8 mM ZnTPP in toluene with 400 nm, 350 µW pump pulses.

Figure 6.5: Transient absorbance of toluene, pumped with 400 nm, 350 µW pulses at selected wavelengths. The non-linear artefact centred on time-zero is around 300 fs long.
Figure 6.6: Kinetic traces of ZnTPP in toluene at selected wavelengths, along with the fits to each wavelength from a 5-exponential global fit.

Figure 6.7: Kinetic traces of ZnTPP in toluene at selected wavelengths, along with the fits to each wavelength from a 3-exponential global fit.