

Rayleigh Optical Activity

A thesis submitted for the degree of
Doctor of Philosophy

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Declaration

The research described in this thesis is my own, except where otherwise stated.

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Abstract

It was predicted over fifty years ago by Laurence D. Barron and collaborators [1, 2] that an isotropic sample of small chiral molecules should exhibit differential Rayleigh scattering with respect to left- and right-handed circular polarisations of light (Rayleigh optical activity or RayOA). In this thesis, we generalise the theory of RayOA to dense samples and present the first-ever experimental observation of the phenomenon for small chiral molecules, obtained using a bespoke instrument. Our measurements for the enantiomers of α -pinene are in precise agreement with our quantum-chemical predictions, establishing RayOA as a viable new technique in the chiroptical toolkit.

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It's virtually impossible to acknowledge everyone that contributed and supported me to finally complete this PhD work but I'm going to give it the old college try!

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Finally, to my family, my mum, dad (who unfortunately is not with us anymore but would appreciate the fact that I somehow ended up working with lasers and lenses) and sister that supported me since forever and made me who I am today and to my beautiful wife Alina that I met and married during this PhD and I can't wait to have a life and family of our own with, I love you more than words can describe!

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Publications

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- D. McArthur, E. I. Alexakis, A. R. Puente, R. McGonigle, A. J. Love, P. L. Polavarapu, L. D. Barron, L. E. MacKenzie, A. S. Arnold and R. P. Cameron. Observation of Rayleigh optical activity for chiral molecules: a new chiroptical tool. *J. Phys. Chem. A*, 129:11884–11887, 2025.
- A. R. Puente, D. McArthur, E. I. Alexakis, L. E. MacKenzie, R. P. Cameron, L. D. Barron and P. L. Polavarapu. Investigation of the robustness of Rayleigh optical activity for the assignment of absolute configurations of chiral molecules. *J. Phys. Chem. A*, 130:2238–2251, 2026.

Summary

In chapter 1, we provide some introductory information on chirality. We give a brief historical background overview of the topic of molecular chirality and optical activity. We provide the motivation and a brief outline of the experimental work that was undertaken in this PhD thesis. We lay the fundamental theoretical building blocks of optical polarisation, we present the theoretical framework of single molecule Rayleigh Optical Activity (RayOA) scattering up to first order in the multipole expansion and we conclude the chapter by presenting some related (but different) phenomena to RayOA.

In chapter 2, we extend the existing theory of RayOA by accounting for the translational and rotational dynamics of the molecules and adding scattered fields due to different molecules coherently, thus obtaining a more general theory that describes Rayleigh-Brillouin optical activity (RayBOA). Our theory provides expressions for not only the total intensity of the analysed signal but also the underlying frequency spectrum. It is applicable to dilute samples such as rarefied gases as well as dense samples such as neat liquids in which correlations between molecules are important.

In chapter 3, we provide a discussion of different scattering configuration trade offs along with our justifications for choosing the optimal one for our purposes. A comparison of reasonable candidate molecules for RayOA measurements is presented along with the quantum chemistry calculations that were performed for comparison to experiment.

In chapter 4, we lay out our experimental set up for our novel instrument. Detailed parts are described and a clear schematic is provided. A model of the detection train is explicitly described along with insights that informed our choices in the experimental

realisation of these measurements. A methodology is also discussed on how to perform corrections on the measured experimental values to account for optical rotation, racemisation of the samples and instrumental offsets.

In chapter 5, we present our experimental results in depth. We explain our experimental and computational methodologies of dealing with noise in our data. Measurements and plots for the two enantiomers of α -pinene in neat liquid form are provided along with provisional results for samples of tobacco mosaic virus (TMV) and turnip yellow mosaic virus (TYMV) in sodium azide buffer solution.

In chapter 6, we provide a summary of all the work that was done and offer future outlook suggestions along with recommendations for potential extensions of our work.

Contents

List of Figures	xi
List of Tables	xv
1 Introduction	1
1.1 Chirality	1
1.2 Historical Background	2
1.3 Optical polarisation	4
1.3.1 Polarisation ellipse	6
1.3.2 Degree of polarisation	8
1.3.3 Stokes parameters	9
1.3.4 Jones and Mueller formalisms	11
1.4 RayOA: state of the art	16
1.5 Related phenomena	25
1.5.1 Reflection optical activity	25
1.5.2 Tyndall optical activity, Mie optical activity and beyond	26
1.5.3 Nonlinear Rayleigh optical activity	26
2 Theory of Rayleigh-Brillouin Optical Activity Applicable to Chiral Liquids	28
2.1 Introduction	28
2.2 Theory of RayBOA	29
2.2.1 The sample	30

Contents

2.2.2	Incident light	32
2.2.3	Scattered light	33
2.2.4	Analysed signal at the detector	35
2.2.5	Frequency spectrum and total intensity	38
2.2.6	Dimensionless circular spectral and intensity differentials	39
2.3	Toy model	41
2.4	Summary and outlook	45
3	Strategy for First Measurements	47
3.1	Introduction	47
3.2	Choice of laser wavelength, scattering angle and polarisation configuration	47
3.2.1	Laser wavelength	47
3.2.2	Scattering angle	48
3.2.3	Polarisation configuration	48
3.3	Choice of molecule	49
3.4	Initial search and basic estimates	50
3.5	In-depth quantum-chemical calculations for α -pinene	51
4	Design of Dedicated RayOA Instrument	54
4.1	Introduction	54
4.2	Overview	55
4.3	High-precision detection system	58
4.3.1	A and B configurations and operating assumptions	68
4.3.2	‘Single deltas’	71
4.3.3	‘Double deltas’	73
4.3.4	‘Triple deltas’	74
4.4	Summary and outlook	76
5	Measurements of RayOA	77
5.1	Introduction	77
5.2	Small chiral molecules	77

Contents

5.2.1	Instrument control	77
5.2.2	Camera background	78
5.2.3	Data acquisition	80
5.2.4	Laser optical power analysis	81
5.2.5	Noise reduction	84
5.2.6	Post selection	87
5.2.7	Masks	89
5.2.8	‘Single deltas’	91
5.2.9	‘Double deltas’	93
5.2.10	‘Triple deltas’	94
5.3	Viruses	100
5.3.1	Tobacco mosaic virus (TMV)	101
5.3.2	Turnip yellow mosaic virus (TYMV)	104
5.4	Summary of Experimental Work	105
6	Summary and Outlook	108
	Bibliography	111

List of Figures

1.1	The opposite enantiomers of the chiral molecule bromochlorofluoromethane.	3
1.2	The polarisation ellipse is shown here in terms of space-fixed axes x and y . The propagation direction z is pointing out of the plane of the plot. The azimuth and ellipticity angles, θ and η respectively, are shown here along with the polarisation ellipse major axis a and minor axis b . The complex polarisation vector $\tilde{\mathbf{e}}$ is also indicated.	6
1.3	Visual representation of the Poincaré sphere. The equator corresponds to linearly polarised states ($\eta = 0$), the north and south poles correspond to circularly polarised states ($\eta = \pm\pi/4$) and all other points on the surface of the sphere correspond to elliptical polarisation. In this case we have set $\{S_1/S_0, S_2/S_0, S_3/S_0\} = \{1/2, 1/2, 1/\sqrt{2}\}$, corresponding to a right-handed elliptical polarisation.	11
2.1	Our scattering geometry, illustrated for neat (1 <i>R</i> ,5 <i>R</i>)- α -pinene and an SCP configuration.	29
2.2	Circular spectra predicted for a toy model of an enantiopure neat liquid. The red and blue curves correspond to opposite enantiomers.	44
4.1	Overview of our instrument. Abbreviations are HWP: half-wave plate, PBS: polarising beam-splitter, LP: linear polariser, QWP: quarter-wave plate, WP: Wollaston prism, CAM: sCMOS camera sensor	55

List of Figures

4.2	Laser power at the transmission and reflection ports of the beam splitter as a function of the half-wave plate angle. The 5° angular offset is due to the mismatch of the HWP axis with the angle markings on the rotation mount and the slight deviation from Malus' law in the transmitted power curve might be due to the beam wandering off the power meter.	56
4.3	Simplified overview of our detection train setup. A rotatable quarter-wave plate (QWP) followed by an independently rotatable Wollaston prism (WP) that "splits" the beam into two mutually orthogonally polarised beams and finally a camera (CAM) for detection. Note that the two lenses in between the WP and the CAM used to focus the diverging beams onto the sensor have been omitted in this figure for the sake of simplicity along with all the light shielding that was used in the actual setup.	59
5.1	Mean and standard deviation background images obtained on a per-pixel basis from 100 dark images, each with an $\Delta t = 30$ s exposure time. The units of the horizontal and vertical axes are number of pixels and the units of the colour bars are 16-bit pixel counts.	79
5.2	Raw, cropped scattered light image of $(1R, 5R)$ - α -pinene. The two spots have been tightly focused in small regions to minimise errors and maximise the SNR. The units of the horizontal and vertical axes are number of pixels and the units of the colour bars are 16-bit pixel counts. Image dimensions: 2160×2100 pixels.	81
5.3	Scatter plots of the normalised laser power $\langle \ell \rangle_n$ versus exposure number n for representative measurement runs on the enantiomers of α -pinene. Red and blue correspond to the A and B configurations of our instrument, with post-selected data points highlighted in vivid colours and the remaining data points rendered in misty colours.	83

List of Figures

5.4	Averaged images of the $+$ signal at three different stages of processing; raw data, background subtracted data on a per-pixel basis, and background subtracted data with additional median filtering with a 3×3 kernel. Images shown are 100×100 pixels with the instrument in the A configuration for $(1S, 5S)$ - α -pinene	86
5.5	Total measured signal $(\langle I_+ \rangle_n + \langle I_- \rangle_n) / \langle \ell \rangle_n$ versus exposure number n for measurement runs on the enantiomers of α -pinene, with normalisation by $\langle \ell \rangle_n$ to correct for laser fluctuations. The oscillatory variation of $\sim 2\text{-}3\%$ seen for the measurement run on $(1S, 5S)$ might be due to modulation of the servo mechanism in the laser responsible for optical power output stability. However, this is largely mitigated by the post selection procedure.	88
5.6	A selection of pixel percentage masks for a measurement run on $(1S, 5S)$ - α -pinene. The larger the pixel percentage, the larger the number of pixels that are included in the calculation of the $\pm$ signals. For pixel percentages over 90%, the masks form a non-contiguous shape that includes unwanted contributions due to the fluorescence “ghost”.	90
5.7	Flow chart of analysis pipeline from importing raw data (green) to final calculations (red).	91
5.8	Plots of $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus exposure number n . Red and blue correspond to the A and B configurations of our instrument, with post-selected data points highlighted in vivid colours and the remaining data points rendered in misty colours.	92
5.9	‘Double deltas’ $\Delta\Delta$ versus pixel percentage for a pair of measurement runs on the enantiomers of α -pinene. Our final measurements come from the 85% – 86% range of interest as labelled. Note that average of the $\Delta\Delta$ values in this range is essentially zero, corresponding to a vanishing instrumental offset $\Delta\Delta_{\text{offset}}$	94
5.10	Instrumental offset $\Delta\Delta_{\text{offset}}$ versus mask pixel percentage.	98

List of Figures

5.11	‘Triple deltas’ $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ versus mask pixel percentage for a pair of measurement runs on the enantiomers of α -pinene.	99
5.12	Measured ‘triple delta’ values $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ for the enantiomers of α -pinene (see black data points at $\lambda = 532$ nm). Also, quantum chemistry predictions for six different density functionals at the aug-cc-pVTZ basis set as a function of wavelength are plotted. The geometry optimisation was the same for all density functionals (B3LYP/6-311G++(d,p)) and was obtained from Autschbach’s OR45 benchmark [123].	100
5.13	TEM analysis of isolated TMV derived structures. Images courtesy of Prof. Andrew Love from the James Hutton Institute.	101
5.14	‘Double delta’ $\Delta\Delta$ vs pixel percentage for a measurement run on TMV.	102
5.15	Diagnostics for a measurement run on TMV. (a): Normalised laser power $\langle\ell\rangle_n$ versus exposure number n . (b): ‘Single deltas’ $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus n . (c): Total measured signal $(\langle I_+\rangle_n + \langle I_-\rangle_n)/\langle\ell\rangle_n$ versus n , normalised by $\langle\ell\rangle_n$ to correct for laser fluctuations.	103
5.16	TEM analysis of isolated TYMV derived structures. Images courtesy of Prof. Andrew Love from the James Hutton Institute.	104
5.17	‘Double delta’ $\Delta\Delta$ versus pixel percentage for a measurement run on TYMV.	105
5.18	Diagnostics for a measurement run on TYMV. (a): Normalised laser power $\langle\ell\rangle_n$ versus exposure number n . (b): ‘Single deltas’ $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus n . (c): Total measured signal $(\langle I_+\rangle_n + \langle I_-\rangle_n)/\langle\ell\rangle_n$ versus n , normalised by $\langle\ell\rangle_n$ to correct for laser fluctuations.	106

List of Tables

1.1	Circular intensity differential coefficients for some important SCP, ICP and DCP _I configurations. The N results are averages of the relevant H and V results, the N standing for “natural” (unpolarised incident light or unanalysed scattered light). Note that the entries in rows one through three and eight through eleven match the entries in rows four through six and twelve through fourteen respectively, in accord with the principle of reciprocity [28, 50–52].	24
2.1	Circular spectral differential coefficients for some important SCP, ICP and DCP _I configurations. The N results are averages of the relevant H and V results, the N standing for “natural” (unpolarised incident light or unanalysed scattered light). Note that the entries in rows one through three and eight through eleven match the entries in rows four through six and twelve through fourteen respectively, in accord with the principle of reciprocity [28, 50–52].	39
3.1	Phase and solubility information and basic estimates of the circular intensity differential Δ for a variety of candidate molecules. Molecular geometries were first optimised at the B3LYP/6-311++G(d,p) level of theory and the tensor components were calculated with uHF-6-311++G(d,p). .	50

3.2	RayOA circular intensity differentials and invariants for (1 <i>R</i> ,5 <i>R</i>)- α -pinene at $\lambda = 532$ nm, computed with six density functionals (Gaussian 16) at the aug-cc-pVTZ basis set in the gas phase. For all these calculations, the α -pinene geometry was optimised at the B3LYP/6-311++G(d,p) level. Listed quantities are the circular intensity differential Δ , the Rayleigh scattering invariants α^2 and β^2 and the RayOA invariants $\alpha G'$, β_G^2 and β_A^2 . Note that Δ is dimensionless and the invariants come by default in Hartree atomic units from Gaussian 16.	53
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Chapter 1

Introduction

1.1 Chirality

Chirality is the property of an object, or a set of points, that cannot be superposed on its mirror image [3]. It is an ever-present phenomenon in the physical world [4], manifesting at all scales. At the subatomic scale, the weak nuclear force interacts exclusively with left-handed particles [5–7]. At the molecular scale, the two mirror-image forms or enantiomers of a chiral molecule can interact in radically different ways with living organisms [8, 9]. At the macroscopic and even cosmic scale, it is visible in the sense of coiling in garden snail shells [10] and in the helical trajectories traced out by the arms of spiral galaxies [11]. Fig. 1.1 shows a visualisation of the two enantiomers of the chiral molecule bromochlorofluoromethane superimposed on human hands.

Chirality is also a defining property of biological organisms, with the amino acids and sugars that comprise the proteins and nucleic acids of life being almost exclusively found in a single enantiomeric form. The interaction of this homochiral chemistry with external chiral compounds leads to distinct outcomes based on the chirality of the latter. An interesting example is the antidepressant citalopram, which is usually sold as a racemic (50/50) mixture of the (*R*)- and (*S*)-enantiomers. The (*S*)-enantiomer is estimated to be up to 10 times more potent than the (*R*)-enantiomer and is marketed separately as escitalopram [9]. It is, therefore, apparent that the ability to distinguish

and quantify enantiomers is of great importance in the pharmaceutical, agrochemical, cosmetics, flavour and fragrance industries (among others). It is estimated that the global market value of chiral compounds currently exceeds 100 billion dollars annually [12, 13].

Despite this importance, the chiroptical techniques that have been most commonly used so far for this purpose date back to the 19th century. The two major ones are optical rotation (OR), i.e. the rotation of linearly polarised light as it travels through a chiral medium due to circular birefringence and circular dichroism (CD), i.e. the differential absorption of left- and right-handed circularly polarised light by a chiral medium. While these techniques have been incredibly successful and they have been refined over the years, they have limitations and certain tasks such as the assignment of absolute configuration remain challenging.

The work presented here aims to add a new chiroptical tool to this arsenal of existing techniques, namely Rayleigh optical activity (RayOA), a linear effect that can be in-principle measured with a simple, inexpensive setup. RayOA is the differential Rayleigh (elastic) scattering of left- and right-handed circularly polarised light, exhibited naturally by isotropic samples of chiral molecules. It probes a different aspect of light-matter interactions (scattering-based) compared to the already established refraction- and absorption-based methods mentioned above, and so could prove uniquely useful for certain tasks such as the assignment of absolute configuration [14].

1.2 Historical Background

François Arago was the first to report optical rotation from a quartz crystal in 1811 [15]. A few years later, Jean-Baptiste Biot reported a similar effect from organic liquid solutions and turpentine [16, 17]. With his systematic measurements, he was able to show that optical rotation was a reproducible property and it could be described as a function of solution concentration and path length.

Around the same period, Augustin-Jean Fresnel was working on polarised light. He was experimenting on total internal reflection (TIR) while using a type of coupled

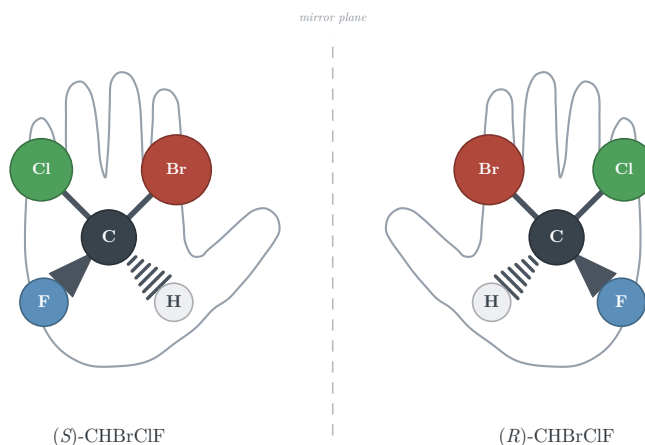


Figure 1.1: The opposite enantiomers of the chiral molecule bromochlorofluoromethane.

glass prism (now known as a Fresnel rhomb) and was able to impose relative phase shifts between orthogonal components of linearly polarised light, generating elliptical and circular polarisation states which are chiral [18]. Writing to the French Academy of sciences in an 1822 memoir, he was the first to correctly describe optical rotation in terms of left- and right-handed circular polarisation [19].

Louis Pasteur was the first to show a connection between these polarisation effects and molecular chirality in 1848 [20]. Pasteur was working with sodium ammonium paratartrate crystals when he noticed that they came in two distinct forms, one being the mirror image of the other. He decided to separate them manually using a pair of tweezers and then dissolve them into two separate solution samples which he tested independently and what he found was that they rotated linearly polarised light in opposite directions. But when they were mixed back together in equal amounts, they would once again form the same paratartaric acid that exhibits no optical rotation whatsoever [21]. This led him to the hypothesis that this asymmetry of optical activity must reside at the regime of individual molecules.

A solid theoretical framework explaining these effects was published in 1874 [22, 23] when Jacobus Henricus van 't Hoff and Joseph Achille Le Bel independently of each other proposed the model of the tetrahedral carbon atom. In this model, a carbon atom

bonded to four different groups would lead to a tetrahedral molecule without a plane of symmetry. This work ended up strengthening the concept of stereochemistry as a new branch of chemistry. Experimental evidence for this model would come later by the invention of X-ray crystallography by William Henry Bragg and his son William Lawrence Bragg in 1912-13 [24]. A few decades later, the publication of the Cahn-Ingold-Prelog priority rules in 1966 [25] provided the rigid framework for the *R/S* absolute configuration system that is still used today.

Since Arago’s first observation of optical activity in the form of optical rotation (OR), there has been a cascade of other chiroptical techniques developed including electronic circular dichroism (ECD) [26], vibrational circular dichroism (VCD) [27], Raman optical activity (ROA) [2, 28] and chiral microwave 3-wave mixing (CM3WM) [29]. In this thesis, we add a new technique to the chiroptical toolkit, namely Rayleigh optical activity (RayOA). This technique is based on elastic light scattering, thus extending chiral spectroscopy beyond absorption and inelastic scattering and provides access to chiral response mechanisms that are complementary to those probed by ROA.

Throughout this work we operate with time t and Cartesian coordinates x , y and z , with associated unit vectors $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ forming a right-handed orthogonal triad. SI units are used. The Einstein summation convention is always assumed unless stated otherwise. A tilde indicates a complex quantity, an asterisk indicates complex conjugation and a caret indicates a unit vector.

1.3 Optical polarisation

Optical polarisation is one of light’s fundamental properties. It describes the direction of oscillation of its electric field¹. The amplitude and frequency of light determine its intensity and colour respectively while its polarisation is a distinct third feature which provides information on the vector-like nature of light. Studying and manipulating the polarisation of light is essential in multiple fields such as optical metrology [30–33],

¹The electric field is used in the definition of polarisation rather than the magnetic field as it usually dominates light-matter interactions.

Chapter 1. Introduction

telecommunications [34, 35], biomedical imaging [36, 37] etc. That's because polarisation is an independent degree of freedom that provides access to information that intensity measurements alone cannot reveal.

Light is an electromagnetic wave that consists of oscillating electric and magnetic fields that are orthogonal to each other and to the direction of propagation. In the case of a monochromatic plane wave propagating in the z direction in vacuum, the complex electric field can be written as

$$\tilde{\mathbf{E}} = \tilde{\mathbf{E}}^{(0)} e^{i(kz - \omega t)}, \quad (1.1)$$

where $\tilde{\mathbf{E}}^{(0)}$ is the complex vector amplitude of the electric field in the transverse plane, k is the angular wavenumber and $\omega = ck$ is the angular frequency. The physical electric field is retrieved as the real part of the complex field: $\mathbf{E} = \text{Re}(\tilde{\mathbf{E}})$. Note that in later chapters where the experiment is discussed, the light used can best be modelled as a Gaussian mode rather than a plane wave. The detection geometry used however, ensures that the light sampled in the detection path can be locally modelled as a plane wave to a good approximation.

Such a field can be decomposed into two coherent waves linearly polarised in the x and y directions as:

$$\tilde{\mathbf{E}} = \tilde{E}_x \hat{\mathbf{x}} + \tilde{E}_y \hat{\mathbf{y}}, \quad (1.2)$$

The polarisation is then determined by the relative phases and magnitudes of the complex components $\tilde{E}_x$ and $\tilde{E}_y$.

The polarisation state is characterised by a complex unit polarisation vector $\tilde{\mathbf{e}}$ such that:

$$\tilde{\mathbf{E}} = E^{(0)} (\tilde{e}_x \hat{\mathbf{x}} + \tilde{e}_y \hat{\mathbf{y}}) e^{i(kz - \omega t)}, \quad (1.3)$$

where $E^{(0)}$ is the scalar amplitude of the electric field.

1.3.1 Polarisation ellipse

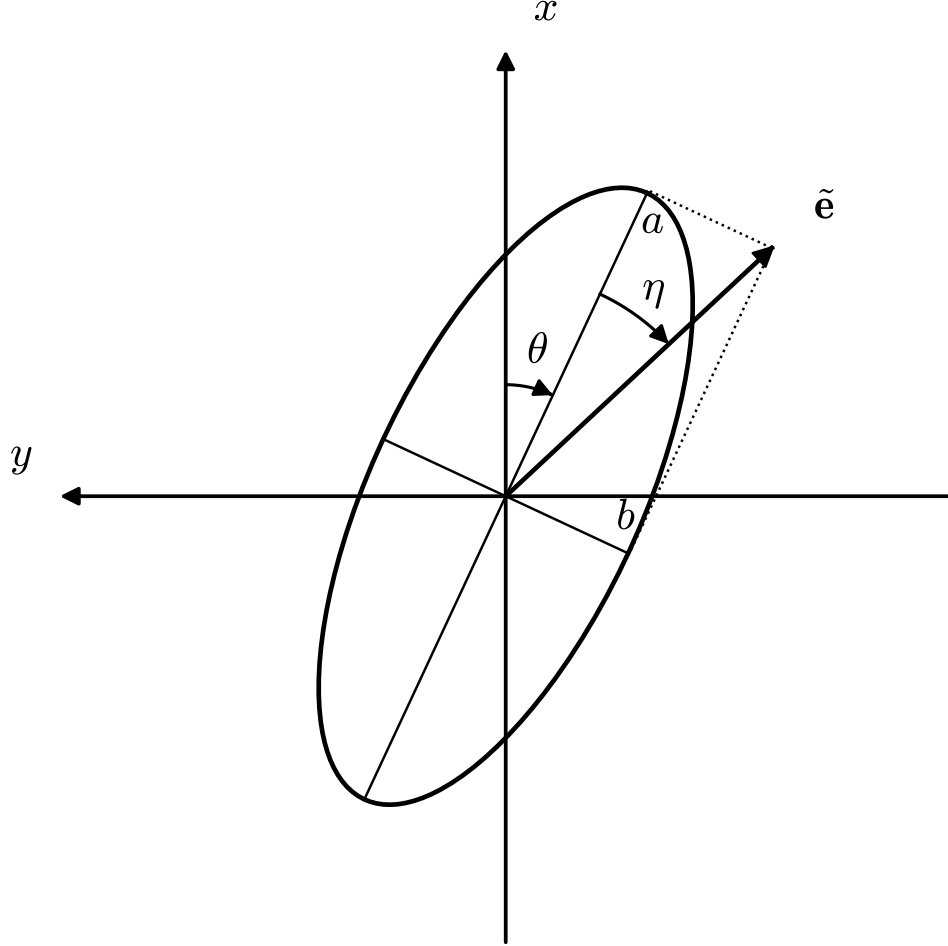


Figure 1.2: The polarisation ellipse is shown here in terms of space-fixed axes x and y . The propagation direction z is pointing out of the plane of the plot. The azimuth and ellipticity angles, θ and η respectively, are shown here along with the polarisation ellipse major axis a and minor axis b . The complex polarisation vector $\tilde{\mathbf{e}}$ is also indicated.

In general, the tip of the electric field vector at a fixed position in space traces out a polarisation ellipse, as shown in Fig. 1.2. The ellipse is defined by two parameters:

Chapter 1. Introduction

- The ellipticity η , defined as:

$$\tan \eta = \frac{b}{a}, \quad (1.4)$$

where b and a are the minor and major axes of the ellipse, respectively, with $-\pi/4 \leq \eta \leq \pi/4$.

- The azimuth θ , which specifies the angle between the major axis and the x -axis, with $0 \leq \theta < 2\pi$.

The complex polarisation vector $\tilde{\mathbf{e}}$ can be expressed in terms of these as

$$\tilde{e}_x = \cos \eta \cos \theta - i \sin \eta \sin \theta \quad (1.5)$$

$$\tilde{e}_y = -\cos \eta \sin \theta - i \sin \eta \cos \theta. \quad (1.6)$$

A positive η corresponds to right-handed ellipticity (clockwise rotation as viewed by an observer receiving the wave), whereas negative η corresponds to left-handed ellipticity. A positive change in θ corresponds to a clockwise or “dextro” rotation of the polarisation ellipse, whereas a negative change in θ corresponds to an anti-clockwise or “laevo” rotation.

The three distinct cases of polarisation are defined as follows:

- **Linear polarisation:** When $\eta = 0$ (i.e. $b = 0$), the electric field oscillates in a straight line that forms an angle θ with the x -axis, the complex electric field being:

$$\tilde{\mathbf{E}}_\theta = E^{(0)}(\cos \theta \hat{\mathbf{x}} - \sin \theta \hat{\mathbf{y}})e^{i(kz - \omega t)}. \quad (1.7)$$

- **Circular polarisation:** When $\eta = \pm\pi/4$ (i.e. $b = a$) and $\theta = 0$, the complex electric field is:

$$\tilde{\mathbf{E}}_{\text{R/L}} = \frac{E^{(0)}}{\sqrt{2}}(\hat{\mathbf{x}} \mp i\hat{\mathbf{y}})e^{i(kz - \omega t)}, \quad (1.8)$$

where R and L denote right and left circular polarisation respectively.

- **Elliptical polarisation:** This is the general case where the electric field vector traces an ellipse with arbitrary azimuth and ellipticity.

1.3.2 Degree of polarisation

A perfectly monochromatic electromagnetic wave like that described above is always completely polarised as the phase relationship and amplitudes of the x and y components of the electric field are strictly defined and remain constant over time. However, many real-life sources of light produce quasi-monochromatic light that contains a small spread of frequencies $\Delta\omega$ centred around ω . In that case, the light can be partially polarised or unpolarised if different frequency components have different polarisation states.

For such quasi-monochromatic light, the electric field at a fixed point can be written as:

$$\tilde{\mathbf{E}} = \tilde{\mathbf{E}}^{(0)}(t)e^{i(kz-\omega t)}, \quad (1.9)$$

where the complex vector amplitude $\tilde{\mathbf{E}}^{(0)}(t) = E^{(0)}(t)\tilde{\mathbf{e}}(t)$ varies with time.

The degree of polarisation P quantifies the fraction of the total intensity that maintains a fixed polarisation state over time and can be defined as:

$$P = \frac{I_{\text{polarised}}}{I_{\text{total}}}, \quad (1.10)$$

where $I_{\text{polarised}}$ is the intensity of the polarised component and I_{total} is the total intensity.

For fully polarised light, the polarisation vector $\tilde{\mathbf{e}}$ is constant over time and $P = 1$. For unpolarised (natural) light, $\tilde{\mathbf{e}}(t)$ fluctuates randomly over time with no preferred azimuth or ellipticity, thus resulting in $P = 0$. In partially polarised light, the degree of polarisation lies in the range $0 < P < 1$ and the light can be decomposed into a fully polarised component with fixed η and θ and an unpolarised component with randomly fluctuating polarisation.

1.3.3 Stokes parameters

A useful concept to describe optical polarisation are the Stokes parameters [38]. These give a complete description of the state of polarisation in terms of measurable intensities. For the wave shown in (1.9), the Stokes parameters can be written as:

$$\begin{aligned} S_0 &= \langle |\tilde{E}_x|^2 \rangle + \langle |\tilde{E}_y|^2 \rangle \\ &= E^{(0)2}, \end{aligned} \quad (1.11)$$

$$\begin{aligned} S_1 &= \langle |\tilde{E}_x|^2 \rangle - \langle |\tilde{E}_y|^2 \rangle \\ &= PE^{(0)2} \cos(2\eta) \cos(2\theta), \end{aligned} \quad (1.12)$$

$$\begin{aligned} S_2 &= -2\text{Re}(\langle \tilde{E}_x \tilde{E}_y^* \rangle) \\ &= PE^{(0)2} \cos(2\eta) \sin(2\theta), \end{aligned} \quad (1.13)$$

$$\begin{aligned} S_3 &= 2\text{Im}(\langle \tilde{E}_x \tilde{E}_y^* \rangle) \\ &= PE^{(0)2} \sin(2\eta), \end{aligned} \quad (1.14)$$

where the angular brackets $\langle \cdot \rangle$ denote time averaging. Each Stokes parameter corresponds to a measurable quantity:

1. S_0 is proportional to the total intensity.
2. S_1 is proportional to the intensity difference between vertically polarised ($\theta = 0$) and horizontally polarised ($\theta = \pi/2$) light.
3. S_2 is proportional to the intensity difference between diagonally polarised ($\theta = 45^\circ$) and antidiagonally polarised ($\theta = -45^\circ$) light.
4. S_3 is proportional to the intensity difference between right-circularly polarised ($\eta = \pi/4$) and left-circularly polarised ($\eta = -\pi/4$) light.

It follows from (1.11)-(1.14) that the degree of polarisation can be expressed in terms of the Stokes parameters as:

$$P = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0}. \quad (1.15)$$

Chapter 1. Introduction

When the light is completely polarised ($P = 1$), only three of the Stokes parameters are independent and this can be expressed as:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2, \quad (1.16)$$

as follows from (1.15).

The normalised Stokes parameters S_1/S_0 , S_2/S_0 and S_3/S_0 can be represented in terms of a unit sphere called a Poincaré sphere, which can be thought of as the equivalent of the Bloch sphere but for light polarisation instead of quantum mechanical states. As we can see in Fig. 1.3, the equator of the Poincaré sphere corresponds to linear polarisation states ($\eta = 0$), the north and south poles correspond to circular polarisation ($\eta = \pm\pi/4$) and all other points on the surface of the sphere correspond to elliptical polarisation. Points inside the sphere correspond to partially polarised light ($0 < P < 1$) with the origin corresponding to completely unpolarised light ($P = 0$).

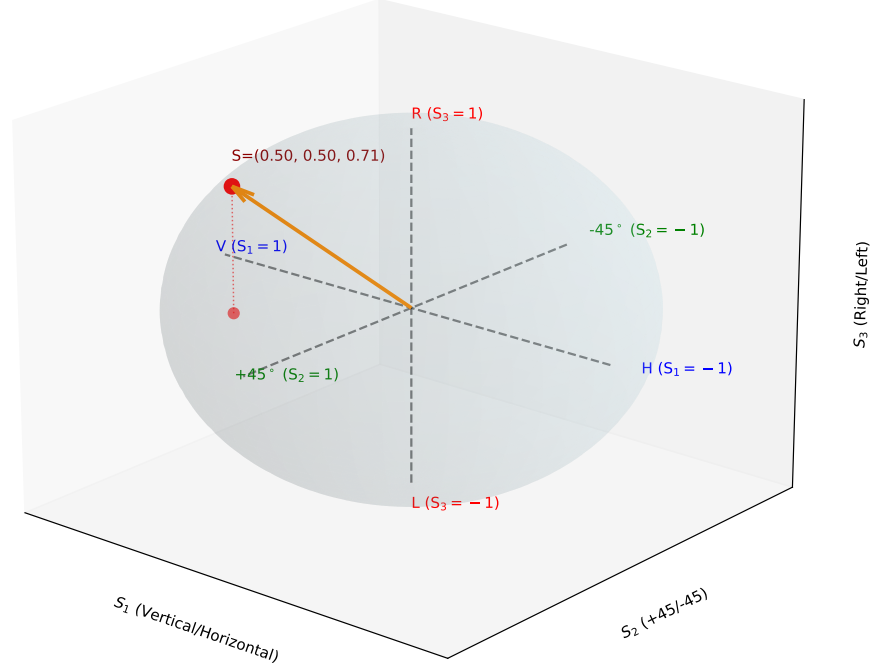


Figure 1.3: Visual representation of the Poincaré sphere. The equator corresponds to linearly polarised states ($\eta = 0$), the north and south poles correspond to circularly polarised states ($\eta = \pm\pi/4$) and all other points on the surface of the sphere correspond to elliptical polarisation. In this case we have set $\{S_1/S_0, S_2/S_0, S_3/S_0\} = \{1/2, 1/2, 1/\sqrt{2}\}$, corresponding to a right-handed elliptical polarisation.

1.3.4 Jones and Mueller formalisms

Light propagation through various optical elements (linear polarisers, waveplates etc.) can be described using matrices that relate the polarisation states of the incident and transmitted light. Two different approaches are commonly used for this purpose: one is Jones calculus, which operates on the electric field amplitudes and is applicable only to fully polarised light, and the other is Mueller calculus, which operates on intensities and can handle arbitrary states of polarisation including partially polarised and unpolarised light.

Jones calculus was introduced by Robert Clark Jones in 1941 [39]; it represents the

polarisation state of a monochromatic plane wave with a spinor-like, complex vector called the Jones vector. For an incident wave propagating in the z direction, the complex electric field $\tilde{\mathbf{E}}$ can be written as:

$$\begin{aligned} \begin{pmatrix} \tilde{E}_x \\ \tilde{E}_y \end{pmatrix} &= \begin{pmatrix} E^{(0)} \tilde{e}_x e^{i(kz-\omega t)} \\ E^{(0)} \tilde{e}_y e^{i(kz-\omega t)} \end{pmatrix} \\ &= E^{(0)} \begin{pmatrix} \tilde{e}_x \\ \tilde{e}_y \end{pmatrix} e^{i(kz-\omega t)} \end{aligned} \quad (1.17)$$

with the Jones vector of the wave being defined up to an overall amplitude and phase factor as

$$\tilde{E} \propto \begin{pmatrix} \tilde{e}_x \\ \tilde{e}_y \end{pmatrix}. \quad (1.18)$$

The effect of an optical element on the polarisation state of the wave can then be described by a 2×2 complex Jones matrix $\tilde{J}$ with the Jones vector $\tilde{E}'$ of the transmitted wave being given by

$$\tilde{E}' = \tilde{J} \tilde{E}. \quad (1.19)$$

Jones calculus is very effective at modelling fully polarised light propagating through an optical system but it falls short in more complicated cases where one has to deal with superpositions of time-varying polarisation vectors leading to partially polarised or unpolarised light.

This is where the second formalism comes in, i.e Mueller calculus, introduced by Hans Mueller in 1943 [40, 41]. This framework can fully tackle an arbitrary degree of polarisation, as it operates on the Stokes parameters which correspond to intensities instead of the electric fields. Therefore, instead of a two-component Jones vector, a four-component Stokes vector S is used with the Stokes parameters as its components

Chapter 1. Introduction

like so:

$$S = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix}. \quad (1.20)$$

This Stokes vector is transformed by a 4×4 Mueller matrix M that corresponds to an optical element like so:

$$S' = MS. \quad (1.21)$$

The ability to handle partially polarised and unpolarised light using the Stokes formalism comes with the trade-off of losing the phase information present in the Jones formalism, as we are no longer dealing with the fields themselves.

Given a Jones matrix of the form

$$\tilde{J} = \begin{pmatrix} \tilde{J}_{xx} & \tilde{J}_{xy} \\ \tilde{J}_{yx} & \tilde{J}_{yy} \end{pmatrix} \quad (1.22)$$

it can be shown that the corresponding Mueller matrix has the form

$$M = \begin{pmatrix} M_{00} & M_{01} & M_{02} & M_{03} \\ M_{10} & M_{11} & M_{12} & M_{13} \\ M_{20} & M_{21} & M_{22} & M_{23} \\ M_{30} & M_{31} & M_{32} & M_{33} \end{pmatrix} \quad (1.23)$$

Chapter 1. Introduction

with elements given by

$$M_{00} = \frac{1}{2}[(\tilde{J}_{xx}\tilde{J}_{xx}^* + \tilde{J}_{xy}\tilde{J}_{xy}^*) + (\tilde{J}_{yx}\tilde{J}_{yx}^* + \tilde{J}_{yy}\tilde{J}_{yy}^*)], \quad (1.24)$$

$$M_{01} = \frac{1}{2}[(\tilde{J}_{xx}\tilde{J}_{xx}^* - \tilde{J}_{xy}\tilde{J}_{xy}^*) + (\tilde{J}_{yx}\tilde{J}_{yx}^* - \tilde{J}_{yy}\tilde{J}_{yy}^*)], \quad (1.25)$$

$$M_{02} = \frac{1}{2}[(-\tilde{J}_{xx}\tilde{J}_{xy}^* - \tilde{J}_{xy}\tilde{J}_{xx}^*) + (-\tilde{J}_{yx}\tilde{J}_{yy}^* - \tilde{J}_{yy}\tilde{J}_{yx}^*)], \quad (1.26)$$

$$M_{03} = \frac{1}{2}[(i\tilde{J}_{xx}\tilde{J}_{xy}^* - i\tilde{J}_{xy}\tilde{J}_{xx}^*) + (i\tilde{J}_{yx}\tilde{J}_{yy}^* - i\tilde{J}_{yy}\tilde{J}_{yx}^*)], \quad (1.27)$$

$$M_{10} = \frac{1}{2}[(\tilde{J}_{xx}\tilde{J}_{xx}^* + \tilde{J}_{xy}\tilde{J}_{xy}^*) - (\tilde{J}_{yx}\tilde{J}_{yx}^* + \tilde{J}_{yy}\tilde{J}_{yy}^*)], \quad (1.28)$$

$$M_{11} = \frac{1}{2}[(\tilde{J}_{xx}\tilde{J}_{xx}^* - \tilde{J}_{xy}\tilde{J}_{xy}^*) - (\tilde{J}_{yx}\tilde{J}_{yx}^* - \tilde{J}_{yy}\tilde{J}_{yy}^*)], \quad (1.29)$$

$$M_{12} = \frac{1}{2}[(-\tilde{J}_{xx}\tilde{J}_{xy}^* - \tilde{J}_{xy}\tilde{J}_{xx}^*) - (-\tilde{J}_{yx}\tilde{J}_{yy}^* - \tilde{J}_{yy}\tilde{J}_{yx}^*)], \quad (1.30)$$

$$M_{13} = \frac{1}{2}[(i\tilde{J}_{xx}\tilde{J}_{xy}^* - i\tilde{J}_{xy}\tilde{J}_{xx}^*) - (i\tilde{J}_{yx}\tilde{J}_{yy}^* - i\tilde{J}_{yy}\tilde{J}_{yx}^*)], \quad (1.31)$$

$$M_{20} = \frac{1}{2}[(-\tilde{J}_{xx}\tilde{J}_{yx}^* + \tilde{J}_{xy}\tilde{J}_{yy}^*) - (\tilde{J}_{yx}\tilde{J}_{xx}^* + \tilde{J}_{yy}\tilde{J}_{xy}^*)], \quad (1.32)$$

$$M_{21} = \frac{1}{2}[(-\tilde{J}_{xx}\tilde{J}_{yx}^* - \tilde{J}_{xy}\tilde{J}_{yy}^*) - (\tilde{J}_{yx}\tilde{J}_{xx}^* - \tilde{J}_{yy}\tilde{J}_{xy}^*)], \quad (1.33)$$

$$M_{22} = \frac{1}{2}[(-\tilde{J}_{xx}\tilde{J}_{yy}^* - \tilde{J}_{xy}\tilde{J}_{yx}^*) - (-\tilde{J}_{yx}\tilde{J}_{xy}^* - \tilde{J}_{yy}\tilde{J}_{xx}^*)], \quad (1.34)$$

$$M_{23} = \frac{1}{2}[-(i\tilde{J}_{xx}\tilde{J}_{yy}^* - i\tilde{J}_{xy}\tilde{J}_{yx}^*) - (i\tilde{J}_{yx}\tilde{J}_{xy}^* - i\tilde{J}_{yy}\tilde{J}_{xx}^*)], \quad (1.35)$$

$$M_{30} = \frac{1}{2}[-i(\tilde{J}_{xx}\tilde{J}_{yx}^* + \tilde{J}_{xy}\tilde{J}_{yy}^*) + i(\tilde{J}_{yx}\tilde{J}_{xx}^* + \tilde{J}_{yy}\tilde{J}_{xy}^*)], \quad (1.36)$$

$$M_{31} = \frac{1}{2}[-i(\tilde{J}_{xx}\tilde{J}_{yx}^* - \tilde{J}_{xy}\tilde{J}_{yy}^*) + i(\tilde{J}_{yx}\tilde{J}_{xx}^* - \tilde{J}_{yy}\tilde{J}_{xy}^*)], \quad (1.37)$$

$$M_{32} = \frac{1}{2}[-i(-\tilde{J}_{xx}\tilde{J}_{yy}^* - \tilde{J}_{xy}\tilde{J}_{yx}^*) + i(-\tilde{J}_{yx}\tilde{J}_{xy}^* - \tilde{J}_{yy}\tilde{J}_{xx}^*)] \quad (1.38)$$

$$M_{33} = \frac{1}{2}[-i(i\tilde{J}_{xx}\tilde{J}_{yy}^* - i\tilde{J}_{xy}\tilde{J}_{yx}^*) + i(i\tilde{J}_{yx}\tilde{J}_{xy}^* - i\tilde{J}_{yy}\tilde{J}_{xx}^*)]. \quad (1.39)$$

Equations (1.24)-(1.39) can be expressed more compactly as

$$M = \tilde{A}(\tilde{J} \otimes \tilde{J}^*)\tilde{A}^{-1}, \quad (1.40)$$

where

$$\tilde{A} = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & -1 & -1 & 0 \\ 0 & -i & i & 0 \end{pmatrix} \quad (1.41)$$

is a complex transformation matrix, $\tilde{A}^{-1}$ is its inverse and $\otimes$ denotes the Kronecker or tensor product.

If we actively rotate an optical field about the $+z$ axis through an angle φ according to the left-hand rule, the Jones and Mueller vectors transform as

$$\tilde{E}(\varphi) = R(\varphi)\tilde{E} \quad (1.42)$$

$$S(\phi) = Q(\varphi)S \quad (1.43)$$

with

$$R(\varphi) = \begin{pmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{pmatrix} \quad (1.44)$$

$$Q(\varphi) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\varphi) & -\sin(2\varphi) & 0 \\ 0 & \sin(2\varphi) & \cos(2\varphi) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (1.45)$$

where $R(\varphi)$ and $Q(\varphi)$ are rotation matrices. If we actively rotate an optical element about the $+z$ axis through an angle φ according to the left-hand rule, the Jones and Mueller matrices transform as

$$\tilde{J}(\varphi) = R(\varphi)\tilde{J}R^T(\varphi) \quad (1.46)$$

$$M(\varphi) = Q(\varphi)MQ^T(\varphi). \quad (1.47)$$

Note that $R^T(\varphi) = R^{-1}(\varphi)$ and $Q^T(\varphi) = Q^{-1}(\varphi)$.

1.4 RayOA: state of the art

In this section, we summarise the state of the art with regards to RayOA as it existed at the start of this PhD.

The modern study of chiral light scattering began in 1969 when Laurence Barron and Peter Atkins identified a new light scattering mechanism arising from interference between a chiral molecule’s electric dipole-electric dipole polarisability tensor and its electric dipole-magnetic dipole and electric dipole-electric quadrupole polarisability tensors [1]. The theory behind this effect was developed further by Barron and Buckingham and published in 1971 [2]. The theory predicts that chiral molecules should scatter left- and right-handed circularly polarised light in different intensities.

This light scattering mechanism manifests in two forms: ROA for inelastic scattering and RayOA for elastic scattering. However, while ROA has been developed into a valuable spectroscopic technique for chiral samples [42, 43], RayOA has remained largely overlooked. The aim of this PhD was to rectify this incredible omission.

ROA was observed by Barron, Bogaard and Buckingham only a few years [44] after the initial theoretical prediction [1, 2] and has since been developed into a powerful chiroptical technique. A natural question to ask, therefore, is why experimental observation of RayOA for small chiral molecules had not been reported in the literature until this PhD.

From a certain point of view RayOA can be thought of as a more challenging technique to implement while at the same time providing less information than ROA. Reasons for this include having to account for the coherent scattering that RayOA involves (as opposed to ROA where scattered intensity contributions from different molecules can be summed incoherently), the frequency degeneracy of incident and scattered light that introduces difficulties to distinguish the true signal from stray light, the fact that certain desirable RayOA configurations require isolating only the anisotropic scattering and that requires tiny solid angles of scattered light collection (not the case in ROA)

etc. RayOA is quantified by a single pseudoscalar circular intensity differential at a single wavelength whereas ROA provides a full chiral spectrum comprised of distinct vibrational modes that can provide structural fingerprints of larger biological samples.

In what follows, we summarise Barron’s original theory of RayOA [1, 2, 28] by showing that the interference between the different polarisability tensors mentioned in the above paragraphs leads to a non-zero intensity difference between left- and right-handed scattered light for linearly polarised incident light or in the intensity of scattered light when left- and right-handed light is incident upon a chiral sample in an alternating way (or both at the same time). These differences will be demonstrated through quantities called circular intensity differentials, which will be derived as functions of molecular polarisabilities.

We work semi-classically using the so-called “local multipole approach” [1, 2] to first-order in the multipolar expansion order parameter $\sigma = 1$; terms of order σ^2 and higher are neglected. The calculations are expressed using tensor notation with the Einstein summation convention to be understood for repeated Greek indices $\alpha, \beta, \gamma, \dots \in \{x, y, z\}$.

Consider a single chiral molecule at the origin and illuminated by incident light that is weak, quasi-monochromatic and has been “switched on” adiabatically in the distant past. We take the incident light to have the form

$$\mathbf{E}^i(\mathbf{r}, t) = \text{Re} \left(\tilde{\mathbf{E}}^i(\mathbf{r}, t) e^{-i\omega t} \right) \quad (1.48)$$

$$\mathbf{B}^i(\mathbf{r}, t) = \text{Re} \left(\tilde{\mathbf{B}}^i(\mathbf{r}, t) e^{-i\omega t} \right), \quad (1.49)$$

where $\mathbf{E}^i$ is the electric field, $\mathbf{B}^i$ is the magnetic field, $\tilde{\mathbf{E}}^i$ is the complex electric field, $\tilde{\mathbf{B}}^i$ is the complex magnetic field, the i superscript stands for incident light and $\omega = ck$ is the central angular frequency, k being the associated angular wavenumber. Assuming that the incident light is a plane wave propagating in the z direction, the Stokes parameters

at the position of the molecule ($\mathbf{r} = 0$) are

$$S_0^i = \langle \tilde{E}_x^i(0) \tilde{E}_x^{i*}(0) + \tilde{E}_y^i(0) \tilde{E}_y^{i*}(0) \rangle, \quad (1.50)$$

$$\begin{aligned} S_1^i &= \langle \tilde{E}_x^i(0) \tilde{E}_x^{i*}(0) - \tilde{E}_y^i(0) \tilde{E}_y^{i*}(0) \rangle \\ &= S_0^i P^i \cos(2\eta^i) \cos(2\theta^i), \end{aligned} \quad (1.51)$$

$$\begin{aligned} S_2^i &= \langle -\tilde{E}_x^i(0) \tilde{E}_y^{i*}(0) - \tilde{E}_y^i(0) \tilde{E}_x^{i*}(0) \rangle \\ &= S_0^i P^i \cos(2\eta^i) \sin(2\theta^i), \end{aligned} \quad (1.52)$$

$$\begin{aligned} S_3^i &= \langle -i\tilde{E}_x^i(0) \tilde{E}_y^{i*}(0) + i\tilde{E}_y^i(0) \tilde{E}_x^{i*}(0) \rangle \\ &= S_0^i P^i \sin(2\eta^i), \end{aligned} \quad (1.53)$$

where P^i is the degree of polarisation, η^i is the ellipticity, θ^i is the azimuth and the angular brackets denote a time average.

The incident light induces oscillating multipole moments in the molecule, given by

$$\sigma^1 \tilde{\mu}_\alpha \approx \sigma^0 \tilde{\alpha}_{\alpha\beta} \tilde{E}_\beta^i(0) + \sigma^1 \frac{1}{3} \tilde{A}_{\alpha,\beta\gamma} \partial_\gamma \tilde{E}_\beta^i(0) + \sigma^1 \tilde{G}_{\alpha\beta} \tilde{B}_\beta^i(0), \quad (1.54)$$

$$\sigma^1 \tilde{\Theta}_{\alpha\beta} \approx \sigma^1 \tilde{\mathcal{A}}_{\gamma,\alpha\beta} \tilde{E}_\gamma^i(0) \quad (1.55)$$

$$\sigma^1 \tilde{m}'_\alpha \approx \sigma^1 \tilde{\mathcal{G}}_{\alpha\beta} \tilde{E}_\beta^i(0), \quad (1.56)$$

where $\tilde{\mu}_\alpha$ is the induced electric dipole moment, $\tilde{\Theta}_{\alpha\beta}$ is the induced electric quadrupole moment, $\tilde{m}'_\alpha$ is the induced mechanical magnetic dipole moment, $\tilde{\alpha}_{\alpha\beta}$ is the electric dipole-electric dipole polarisability tensor, $\tilde{G}_{\alpha\beta}$ and $\tilde{\mathcal{G}}_{\alpha\beta}$ are electric dipole-magnetic dipole polarisability tensors (the difference between the two being that the sign of the time-even part is flipped) and $\tilde{\mathcal{A}}_{\gamma,\alpha\beta}$ and $\tilde{A}_{\alpha,\beta\gamma}$ are electric dipole-electric quadrupole polarisability tensors (same as above, the difference between them is an inverted sign on the imaginary part). Note here that $\tilde{m}'_\alpha$ is defined using the kinetic (mechanical) momentum $\mathbf{p}_{\text{mech}} = \mathbf{p}_{\text{can}} - q\mathbf{A}$ rather than the canonical momentum $\mathbf{p}_{\text{can}}$, where q is the electric charge of a particle in the molecule and $\mathbf{A}$ is the vector potential. As such, $\mathbf{m}' = q\mathbf{r} \times (\mathbf{p}_{\text{can}} - q\mathbf{A})/2m$ contains both a paramagnetic (first term) and a diamagnetic (second term) contribution, m being the particle's mass.

Chapter 1. Introduction

These oscillating multipole moments generate scattered light of the form

$$\mathbf{E}^s(\mathbf{r}, t) = \Re \left(\tilde{\mathbf{E}}^s(\mathbf{r}) e^{-i\omega t} \right) \quad (1.57)$$

$$\mathbf{B}^s(\mathbf{r}, t) = \Re \left(\tilde{\mathbf{B}}^s(\mathbf{r}) e^{-i\omega t} \right), \quad (1.58)$$

with

$$\tilde{E}_\alpha^s = \frac{\mu_0 \omega^2 e^{ikr}}{4\pi r} (\delta_{\alpha\beta} - \hat{r}_\alpha \hat{r}_\beta) \left(\sigma^0 \tilde{\mu}_\beta + \sigma^1 \frac{1}{c} \epsilon_{\beta\gamma\delta} \tilde{m}'_\gamma \hat{r}_\delta - \sigma^1 \frac{ik}{3} \tilde{\Theta}_{\beta\gamma} \hat{r}_\gamma \right) \quad (1.59)$$

$$\tilde{B}_\alpha^s = \frac{1}{c} \epsilon_{\alpha\beta\gamma} \hat{r}_\beta \tilde{E}_\gamma^s, \quad (1.60)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta, $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor, the s superscript stands for scattered light and the angular frequency ω is the same as that of the incident light as we are considering elastic light scattering. Substituting (1.54)-(1.56) into (1.59), we obtain the more explicit form

$$\begin{aligned} \tilde{E}_\alpha^s = \frac{\mu_0 \omega^2 e^{ikr}}{4\pi r} (\delta_{\alpha\beta} - \hat{r}_\alpha \hat{r}_\beta) & \left(\sigma^0 \tilde{\alpha}_{\beta\gamma} \tilde{E}_\gamma^i + \sigma^1 \frac{1}{3} \tilde{A}_{\beta,\delta\gamma} \partial_\gamma \tilde{E}_\delta^i + \sigma^1 \tilde{G}_{\beta\gamma} \tilde{B}_\gamma^i \right. \\ & \left. + \sigma^1 \frac{1}{c} \epsilon_{\beta\gamma\delta} \tilde{\mathcal{G}}_{\gamma\epsilon} \tilde{E}_\epsilon^i \hat{r}_\delta - \sigma^1 \frac{ik}{3} \tilde{\mathcal{A}}_{\delta,\beta\gamma} \tilde{E}_\delta^i \hat{r}_\gamma \right), \end{aligned} \quad (1.61)$$

which expresses the scattered light in terms of the molecule's polarisability tensors and the incident light.

Taking $x = 0$ to be the scattering plane and ξ to be the scattering angle measured from the z direction, the Stokes parameters of the scattered light are given by

$$\begin{aligned} S_0^s &= \langle \tilde{E}_x^s \tilde{E}_x^{s*} \rangle + \cos^2 \xi \langle \tilde{E}_y^s \tilde{E}_y^{s*} \rangle \\ &\quad - \sin \xi \cos \xi (\langle \tilde{E}_y^s \tilde{E}_z^{s*} \rangle + \langle \tilde{E}_z^s \tilde{E}_y^{s*} \rangle) + \sin^2 \xi \langle \tilde{E}_z^s \tilde{E}_z^{s*} \rangle, \end{aligned} \quad (1.62)$$

$$\begin{aligned} S_1^s &= \langle \tilde{E}_x^s \tilde{E}_x^{s*} \rangle - \cos^2 \xi \langle \tilde{E}_y^s \tilde{E}_y^{s*} \rangle \\ &\quad + \sin \xi \cos \xi (\langle \tilde{E}_y^s \tilde{E}_z^{s*} \rangle + \langle \tilde{E}_z^s \tilde{E}_y^{s*} \rangle) - \sin^2 \xi \langle \tilde{E}_z^s \tilde{E}_z^{s*} \rangle, \end{aligned} \quad (1.63)$$

$$S_2^s = -\cos \xi (\langle \tilde{E}_x^s \tilde{E}_y^{s*} \rangle + \langle \tilde{E}_y^s \tilde{E}_x^{s*} \rangle) + \sin \xi (\langle \tilde{E}_x^s \tilde{E}_z^{s*} \rangle + \langle \tilde{E}_z^s \tilde{E}_x^{s*} \rangle) \quad (1.64)$$

$$S_3^s = -i \cos \xi (\langle \tilde{E}_x^s \tilde{E}_y^{s*} \rangle - \langle \tilde{E}_y^s \tilde{E}_x^{s*} \rangle) + i \sin \xi (\langle \tilde{E}_x^s \tilde{E}_z^{s*} \rangle - \langle \tilde{E}_z^s \tilde{E}_x^{s*} \rangle), \quad (1.65)$$

Chapter 1. Introduction

As we are usually interested in isotropic samples like a solution or a liquid, we replace the time averages of the molecule's property tensors with rotational averages over all possible orientations of the molecule [45] using

$$\langle \tilde{\alpha}_{\alpha\beta} \tilde{\alpha}_{\gamma\delta}^* \rangle = \frac{1}{30} \begin{bmatrix} \delta_{\alpha\beta} \delta_{\gamma\delta} \\ \delta_{\alpha\gamma} \delta_{\beta\delta} \\ \delta_{\alpha\delta} \delta_{\beta\gamma} \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} \delta_{\alpha'\beta'} \delta_{\gamma'\delta'} \\ \delta_{\alpha'\gamma'} \delta_{\beta'\delta'} \\ \delta_{\alpha'\delta'} \delta_{\beta'\gamma'} \end{bmatrix} \tilde{\alpha}_{\alpha'\beta'} \tilde{\alpha}_{\gamma'\delta'}^*, \quad (1.66)$$

applied on the rank-4 tensor elements $\tilde{\alpha}_{\alpha\beta} \tilde{\alpha}_{\gamma\delta}^*$, $\tilde{\alpha}_{\alpha\beta} \tilde{G}_{\gamma\delta}^*$ and $\tilde{\alpha}_{\alpha\beta} \tilde{\mathcal{G}}_{\gamma\delta}^*$ and

$$\langle \tilde{\alpha}_{\alpha\beta} \tilde{A}_{\gamma,\delta\epsilon}^* \rangle = \frac{1}{30} \begin{bmatrix} \epsilon_{\alpha\beta\gamma} \delta_{\delta\epsilon} \\ \epsilon_{\alpha\beta\delta} \delta_{\gamma\epsilon} \\ \epsilon_{\alpha\beta\epsilon} \delta_{\gamma\delta} \\ \epsilon_{\alpha\gamma\delta} \delta_{\beta\epsilon} \\ \epsilon_{\alpha\gamma\epsilon} \delta_{\beta\delta} \\ \epsilon_{\alpha\delta\epsilon} \delta_{\beta\gamma} \end{bmatrix}^T \begin{bmatrix} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{bmatrix} \begin{bmatrix} \epsilon_{\alpha'\beta'\gamma'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \\ \epsilon_{\alpha'\beta'\delta'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \\ \epsilon_{\alpha'\beta'\epsilon'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \\ \epsilon_{\alpha'\gamma'\delta'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \\ \epsilon_{\alpha'\gamma'\epsilon'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \\ \epsilon_{\alpha'\delta'\epsilon'} \tilde{\alpha}_{\alpha'\beta'} \tilde{A}_{\gamma',\delta'\epsilon'}^* \end{bmatrix}, \quad (1.67)$$

applied on the rank-5 tensor elements $\tilde{\alpha}_{\alpha\beta} \tilde{A}_{\gamma,\delta\epsilon}^*$ and $\tilde{\alpha}_{\alpha\beta} \tilde{\mathcal{A}}_{\gamma,\delta\epsilon}^*$ [46]. Assuming that our scatterer is transparent and diamagnetic such that $\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} = \alpha_{\beta\alpha}$, $\tilde{G}_{\alpha\beta} = -iG'_{\alpha\beta}$, $\tilde{\mathcal{G}}_{\alpha\beta} = iG'_{\beta\alpha}$, $\tilde{A}_{\alpha,\beta\gamma} = A_{\alpha,\beta\gamma}$ and $\tilde{\mathcal{A}}_{\alpha,\beta\gamma} = A_{\alpha,\beta\gamma}$, we then find that the Stokes parameters

Chapter 1. Introduction

of the scattered light are

$$S_0^s(\xi) = K \left\{ \left[\frac{1}{2} (1 + P^i \cos(2\eta^i) \cos(2\theta^i)) + \frac{1}{2} (1 - P^i \cos(2\eta^i) \cos(2\theta^i)) \cos^2 \xi \right] \right. \\ \times \left(30\alpha^2 + \frac{2\beta^2}{3} \right) + 4\beta^2 + \frac{1}{c} P^i \sin(2\eta^i) \left[30\alpha G' + \frac{26}{3} \beta_G^2 - \frac{2}{3} \beta_A^2 \right. \\ \left. \left. + \cos \xi \left(60\alpha G' - \frac{20}{3} \beta_G^2 - 4\beta_A^2 \right) + \cos^2 \xi \left(30\alpha G' + \frac{2}{3} \beta_G^2 + 2\beta_A^2 \right) \right] \right\}, \quad (1.68)$$

$$S_1^s(\xi) = K \left\{ \left[\frac{1}{2} (1 + P^i \cos(2\eta^i) \cos(2\theta^i)) + \frac{1}{2} (-1 + P^i \cos(2\eta^i) \cos(2\theta^i)) \cos^2 \xi \right] \right. \\ \times \left(30\alpha^2 + \frac{2\beta^2}{3} \right) + \frac{1}{c} P^i \sin(2\eta^i) \sin^2 \xi \left(30\alpha G' + \frac{2}{3} \beta_G^2 + 2\beta_A^2 \right) \left. \right\}, \quad (1.69)$$

$$S_2^s(\xi) = K P^i \cos(2\eta^i) \sin(2\theta^i) \left(30\alpha^2 + \frac{2\beta^2}{3} \right) \cos \xi, \quad (1.70)$$

$$S_3^s(\xi) = K \left\{ P^i \sin(2\eta^i) \left(30\alpha^2 - \frac{10\beta^2}{3} \right) \cos \xi + \frac{1}{c} P^i \left[30\alpha G' + \frac{26}{3} \beta_G^2 - \frac{2}{3} \beta_A^2 \right. \right. \\ \left. \left. + \cos \xi \left(60\alpha G' - \frac{20}{3} \beta_G^2 - 4\beta_A^2 \right) + \cos^2 \xi \left(30\alpha G' + \frac{2}{3} \beta_G^2 + 2\beta_A^2 \right) \right] \right. \\ \left. + \frac{1}{c} P^i \cos(2\eta^i) \cos(2\theta^i) \sin^2 \xi \left(30\alpha G' + \frac{2}{3} \beta_G^2 + 2\beta_A^2 \right) \right\}, \quad (1.71)$$

where

$$K = \frac{1}{30} \left(\frac{\mu_0 \omega^2}{4\pi r} \right)^2 S_0^i \quad (1.72)$$

is a shorthand. In (1.68)-(1.71), we have introduced the parameters

$$\alpha^2 = \frac{1}{9} \alpha_{\alpha\alpha} \alpha_{\beta\beta} \quad (1.73)$$

$$\beta^2 = \frac{1}{2} (3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}) \quad (1.74)$$

Chapter 1. Introduction

as well as

$$\alpha G' = \frac{1}{9} \alpha_{\alpha\alpha} G'_{\beta\beta}, \quad (1.75)$$

$$\beta_G^2 = \frac{1}{2} (3\alpha_{\alpha\beta} G'_{\alpha\beta} - \alpha_{\alpha\alpha} G'_{\beta\beta}), \quad (1.76)$$

$$\beta_A^2 = \frac{\omega}{2} \epsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma,\delta\beta}. \quad (1.77)$$

At zeroth order in the multipolar expansion parameter σ , α^2 is the isotropic Rayleigh scattering invariant and is always positive while β^2 is the anisotropic Rayleigh scattering invariant which is typically $\sim \alpha^2/10$ for a small molecule [14]. Therefore, β^2 can be thought of as a measure of anisotropy as it goes to zero for a perfectly isotropic scatterer such as an atom. As for the first order in σ , $\alpha G'$ and β_G^2 are the isotropic and anisotropic RayOA invariants respectively arising from the contraction of the electric dipole-electric dipole tensor $\alpha_{\alpha\beta}$ with the electric dipole-magnetic dipole tensor $G'_{\alpha\beta}$ and β_A^2 is the anisotropic RayOA invariant arising from the contraction of $\alpha_{\alpha\beta}$ with the electric dipole-electric quadrupole tensor $A_{\alpha,\beta\gamma}$. The RayOA invariants $\alpha G'$, β_G^2 and β_A^2 are useful because they have opposite signs for opposite enantiomers, serving as probes of molecular chirality. Individual components of $G'_{\alpha\beta}$ and $A_{\alpha,\beta\gamma}$ are dependent on the choice of origin for multipolar expansions, however when summed over to generate the RayOA invariants $\alpha G'$, β_G^2 and β_A^2 the net results are origin-independent, giving unique physical predictions.

In an actual laboratory measurement of RayOA, a choice needs to be made on the polarisation and angle of scattering used.

In terms of polarisation selection, there are three main choices. The first one is called the incident circular polarisation (ICP) scheme where the sample is illuminated with alternating left- and right-handed circularly polarised light and an intensity difference is measured in the scattered light (usually analysed for the horizontal component for the reduction of polarisation artefacts). This was the approach used by Barron in the first successful detection of ROA from neat 1-phenylethanol and 1-phenylethylamine in 1973 [44].

Chapter 1. Introduction

The second option is the scattered circular polarisation (SCP) scheme where the sample is illuminated by either fixed linearly polarised or completely unpolarised light and the scattered light obtains an ellipticity in the form of a small circularly polarised component. The difference between left- and right-handed circularly polarised scattered light is then observed to produce a measurement. It was first reported experimentally in 1988 for a ROA experiment by Spencer, Freedman and Nafie [47].

The final scattering option is the dual circular polarisation (DCP) scheme where both the incident and scattered light are circularly polarised. This scheme can be subdivided into DCP_I in-phase scattering where incident and scattered light are controlled to be both right-handed or left-handed and DCP_{II} out-of-phase scattering where incident and scattered light are controlled to have opposite circularities. The DCP approach was proposed in 1989 by Nafie and Freedman [48] and first demonstrated for ROA in 1991 by Che, Hecht and Nafie [49].

A further parameter in those schemes is the chosen scattering angle ξ . Popular choices have included forward scattering ($\xi = 0^\circ$), backscattering ($\xi = 180^\circ$), right-angle scattering ($\xi = 90^\circ$) etc. Different angles have different contributions from the optical activity polarisability tensors and therefore lead to different results. We elaborate further on the benefits and drawbacks of these different techniques and scattering angles in chapter 3.

For the special case of a pure, rarefied gas of small chiral molecules, a RayOA measurement can be represented by an intensity difference between left- and right-handed circular polarisation [14] in the three different polarisation schemes mentioned above (ICP, SCP or DCP). This intensity difference can be quantified as a dimensionless circular intensity differential of the form [2]

$$\begin{aligned}\Delta(\xi) &= \frac{I^{\text{ab}}(\xi) - I^{\text{cd}}(\xi)}{I^{\text{ab}}(\xi) + I^{\text{cd}}(\xi)} \\ &\approx \frac{A + B \cos \xi + C \cos^2 \xi}{D + E \cos \xi + F \cos^2 \xi}\end{aligned}\tag{1.78}$$

where I is the intensity of the scattered light, a and c correspond to the polarisation

Chapter 1. Introduction

state of the analysed light, b and d correspond to the polarisation state of the incident light and the coefficients A , B , C , D , E and F are functions of the RayOA invariants that depend on the scattering configuration.

a	b	c	d	$3cA/K$	$3cB/K$	$3cC/K$
R	H	L	H	$24\beta_G^2 - 8\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
R	V	L	V	$180\alpha G' + 28\beta_G^2 + 4\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	0
R	N	L	N	$90\alpha G' + 26\beta_G^2 - 2\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$90\alpha G' + 2\beta_G^2 + 6\beta_A^2$
H	R	H	L	$24\beta_G^2 - 8\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
V	R	V	L	$180\alpha G' + 28\beta_G^2 + 4\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	0
N	R	N	L	$90\alpha G' + 26\beta_G^2 - 2\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$90\alpha G' + 2\beta_G^2 + 6\beta_A^2$
R	R	L	L	$180\alpha G' + 52\beta_G^2 - 4\beta_A^2$	$360\alpha G' - 40\beta_G^2 - 24\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
a	b	c	d	$3D/K$	$3E/K$	$3F/K$
R	H	L	H	$12\beta^2$	0	$90\alpha^2 + 2\beta^2$
R	V	L	V	$90\alpha^2 + 14\beta^2$	0	0
R	N	L	N	$45\alpha^2 + 13\beta^2$	0	$45\alpha^2 + \beta^2$
H	R	H	L	$12\beta^2$	0	$90\alpha^2 + 2\beta^2$
V	R	V	L	$90\alpha^2 + 14\beta^2$	0	0
N	R	N	L	$45\alpha^2 + 13\beta^2$	0	$45\alpha^2 + \beta^2$
R	R	L	L	$45\alpha^2 + 13\beta^2$	$90\alpha^2 - 10\beta^2$	$45\alpha^2 + \beta^2$

Table 1.1: Circular intensity differential coefficients for some important SCP, ICP and DCP_I configurations. The N results are averages of the relevant H and V results, the N standing for “natural” (unpolarised incident light or unanalysed scattered light). Note that the entries in rows one through three and eight through eleven match the entries in rows four through six and twelve through fourteen respectively, in accord with the principle of reciprocity [28, 50–52].

The various intensities in (1.78) can be calculated from the Stokes parameters of the scattered light (1.68)-(1.71).

As an example, let us focus on the SCP scheme with right-angle scattering and horizontal incident polarisation (parallel to the scattering plane). From this, it follows that $P^i = 1$, $\eta^i = 0$, $\theta^i = 90^\circ$ and $\xi = 90^\circ$. Substituting these values into (1.68)-(1.71), we obtain the relevant intensities:

$$I^{\text{RH}}(90^\circ) = \frac{1}{2} [\langle S_0^s \rangle(90^\circ) + \langle S_3^s \rangle(90^\circ)] = \frac{2K}{3c} (3c\beta^2 + 6\beta_G^2 - 2\beta_A^2) \quad (1.79)$$

$$I^{\text{LH}}(90^\circ) = \frac{1}{2} [\langle S_0^s \rangle(90^\circ) - \langle S_3^s \rangle(90^\circ)] = \frac{2K}{3c} (3c\beta^2 - 6\beta_G^2 + 2\beta_A^2). \quad (1.80)$$

With these intensities now derived, we can build the relevant Δ value as follows:

$$I^{\text{RH}} - I^{\text{LH}} = \frac{8K}{3c} (3\beta_G^2 - \beta_A^2), \quad (1.81)$$

$$I^{\text{RH}} + I^{\text{LH}} = 4K\beta^2 \quad (1.82)$$

$$\Delta(90^\circ) = \frac{I^{\text{RH}} - I^{\text{LH}}}{I^{\text{RH}} + I^{\text{LH}}} = \frac{1}{c} \frac{24\beta_G^2 - 8\beta_A^2}{12\beta^2}. \quad (1.83)$$

Table 1.1 summarises some of the most important expressions for the circular intensity differential $\Delta(\xi)$ for all three schemes (ICP, SCP and DCP_{I/II}).

1.5 Related phenomena

We conclude this chapter now by briefly comparing and contrasting RayOA with some closely related but distinct chiroptical phenomena.

1.5.1 Reflection optical activity

RayOA should not be confused with reflection optical activity (RefOA), which is the differential reflection of left- and right-handed circularly polarised light, exhibited naturally by chiral media. The first experimental observation of RefOA was reported by Silverman, Badoz and Briat in 1992 [53] following much theoretical debate about the form of the Fresnel coefficients for chiral media. The original experiment measured differential circular reflection parameters akin to the RayOA circular intensity differential Δ for a solution of camphorquinone in methanol harnessing total internal reflection in favourable single- and double-bounce geometries.

Fundamentally, RayOA and RefOA derive from the same molecular light scattering mechanism [28]. That they are nevertheless distinct phenomena can be appreciated simply by noting that RayOA vanishes for a (hypothetical) perfectly homogeneous sample whilst RefOA persists and conversely that RefOA vanishes in the limit of a rarefied sample whilst RayOA persists.

1.5.2 Tyndall optical activity, Mie optical activity and beyond

For large biological scatterers, the terminology “circular intensity differential scattering” (CIDS) is often used [54–58] for what is otherwise RayOA. The key difference is the size of the scatterer; in CIDS, the scatterer size is comparable or sometimes even larger than the wavelength of light ($d \approx \lambda$) whereas in RayOA the size of the scatterer is much smaller than the wavelength ($d \ll \lambda$). The distinction is important because in CIDS measurements, we are no longer in a Rayleigh scattering regime; more general electromagnetic scattering approaches are used to describe the interaction (like coupled-dipole methods or T -matrix formulations) and different information is usually obtained like the helical pitch of the scatterer. CIDS has been successfully used in probing the supramolecular structure of large biological samples like chromatin, viruses and whole cells. A well-known application of the CIDS technique was the observation of a strong signal from the helical sperm head of the octopus *Eledone cirrhosa* [54], a left-handed helical specimen with pitch and diameter of $\approx 1 \mu\text{m}$.

1.5.3 Nonlinear Rayleigh optical activity

RayOA, a linear process, is not to be confused with hyper Rayleigh optical activity (HRS OA) [59–63] and its extensions [64, 65], which are distinct, nonlinear optical phenomena. In HRS OA, two photons of angular frequency ω interact with the scatterer to produce a scattered photon of double the angular frequency 2ω (the second-harmonic). While RayOA probes the interference between the (linear) electric dipole-electric dipole polarisability tensor α with the electric dipole-magnetic dipole polarisability tensor G' and the electric dipole-electric quadrupole polarisability tensor A , HRS OA probes chiral interferences between (nonlinear) hyperpolarisability tensors. This is a complimentary technique to linear methods as it probes different molecular properties and can reveal chiral information from systems where linear optical activity may be weak. The effect, predicted theoretically in 1979 [59], remained experimentally elusive for about four decades until the first observation in 2019 using silver nanohelices suspended in water [60] and independently using foldamer molecules [61]. Additional measurements have

Chapter 1. Introduction

since been reported for e.g. gold helicoids [62].

Chapter 2

Theory of Rayleigh-Brillouin Optical Activity Applicable to Chiral Liquids

2.1 Introduction

In the theoretical descriptions of RayOA published prior to the start of this PhD, each molecule is effectively held static in position and orientation and scattered intensities due to different molecules are added incoherently [1, 2, 14, 28, 46, 66–71]. These descriptions provide expressions for the total intensity of the analysed signal and are best suited to dilute samples such as rarefied gases in which correlations between molecules are unimportant [28, 72–75].

In this chapter, which is based on our publication [76], we extend the existing theory of RayOA by accounting for the translational and rotational dynamics of the molecules and adding scattered fields due to different molecules coherently, thus obtaining a more general theory that describes Rayleigh-Brillouin optical activity (RayBOA). Our theory provides expressions for not only the total intensity of the analysed signal but also the underlying frequency spectrum. It is applicable to dilute samples such as rarefied gases as well as dense samples such as neat liquids in which correlations between molecules

are important.

The theory of ROA does not need to be extended like the theory of RayOA, as one can add Raman scattered intensities due to different molecules incoherently at essentially all sample densities [28, 77].

In this largely publication-based chapter, my contributions were mainly focused on the choice of the appropriate constitutive relation along with the calculation of chiral-achiral and achiral-achiral pairs in section 2.2.5.

2.2 Theory of RayBOA

Let us consider weak, monochromatic, off-resonant, planar light incident upon a non-conducting fluid of small, diamagnetic, chiral molecules, as illustrated in Fig. 2.1. Fluctuations of the optical properties (e.g. refractive indices) within the scattering volume give rise to Rayleigh-Brillouin scattering away from the forward direction [78–100], a fraction of which is analysed at a detector in the far field. In what follows, we derive expressions for dimensionless circular spectral differentials and dimensionless circular intensity differentials which serve as convenient measures of the Rayleigh-Brillouin optical activity exhibited by the sample.

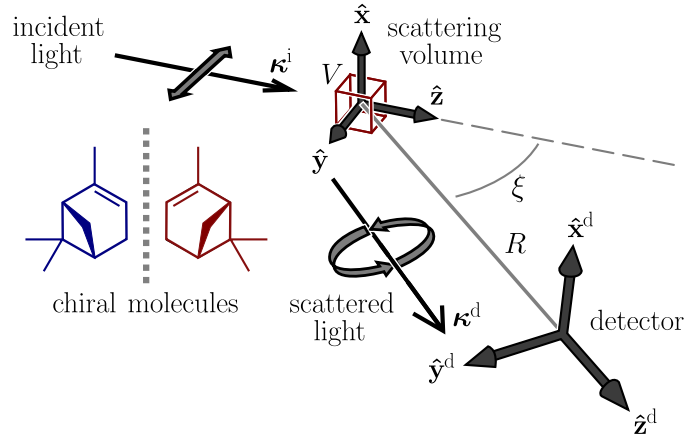


Figure 2.1: Our scattering geometry, illustrated for neat (1*R*,5*R*)- α -pinene and an SCP configuration.

Our derivation borrows heavily from theoretical descriptions of Rayleigh-Brillouin

scattering by Landau and Lifshitz [72] and Berne and Pecora [73] and is essentially an amalgamation of these with Barron’s mechanism of Rayleigh optical activity [1, 2, 28]. See also [101–104]. We work in an inertial frame of reference with time t and position vector $\mathbf{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$, where x , y and z are right-handed Cartesian coordinates and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are the associated unit vectors. The Einstein summation convention is to be understood with respect to unprimed Greek indices $\alpha, \beta, \dots \in \{x, y, z\}$ and primed Greek indices $\alpha', \beta', \dots \in \{X^{(n)}, Y^{(n)}, Z^{(n)}\}$, where $X^{(n)}$, $Y^{(n)}$ and $Z^{(n)}$ are molecule-fixed Cartesian coordinates for the n^{th} molecule. Complex quantities are decorated with tildes and unit vectors are decorated with carets. We use SI units throughout.

2.2.1 The sample

Within the scattering volume V , we model the sample as a collection of vibronically polarisable molecules that can translate with position vectors $\mathbf{R}^{(n)} = \mathbf{R}^{(n)}(t)$ and rotate with Euler angles $\vartheta^{(n)} = \vartheta^{(n)}(t)$, $\varphi^{(n)} = \varphi^{(n)}(t)$ and $\chi^{(n)} = \chi^{(n)}(t)$ ($n \in \{1, \dots\}$) [105]. By “vibronic”, we mean simply that the polarisabilities account for electromagnetic perturbation of the vibrational and electronic degrees of freedom of the molecules. The initial and final states in the polarisabilities are taken to be the same; the molecules do *not* undergo real vibronic transitions. In the interests of generality, we say nothing about the explicit forms of the positions and orientations of the molecules, except that they are such that the sample is optically homogeneous and isotropic on average.

We take the light to satisfy Maxwell’s equations in the form

$$\nabla \cdot \tilde{\mathbf{D}} = 0, \tag{2.1}$$

$$\nabla \cdot \tilde{\mathbf{B}} = 0, \tag{2.2}$$

$$\nabla \times \tilde{\mathbf{E}} = - \frac{\partial \tilde{\mathbf{B}}}{\partial t} \tag{2.3}$$

$$\nabla \times \tilde{\mathbf{B}} = \mu_0 \frac{\partial \tilde{\mathbf{D}}}{\partial t} \tag{2.4}$$

together with the constitutive relation

$$\tilde{\mathbf{D}} \approx \epsilon_0 \tilde{\mathbf{E}} + \tilde{\mathbf{P}} - \frac{1}{i\omega} \nabla \times \tilde{\mathbf{M}}, \quad (2.5)$$

where $\tilde{\mathbf{D}} = \tilde{\mathbf{D}}(\mathbf{r}, t)$, $\tilde{\mathbf{E}} = \tilde{\mathbf{E}}(\mathbf{r}, t)$, $\tilde{\mathbf{B}} = \tilde{\mathbf{B}}(\mathbf{r}, t)$, $\tilde{\mathbf{P}} = \tilde{\mathbf{P}}(\mathbf{r}, t)$ and $\tilde{\mathbf{M}} = \tilde{\mathbf{M}}(\mathbf{r}, t)$ are the complex displacement, electric, magnetic, polarisation and magnetisation fields and ω is the angular frequency of the incident light [28, 46, 106].

Working in the domain of linear optics to first order in multipolar expansions whilst neglecting local field corrections, we take

$$\tilde{P}_\alpha \approx \sum_n \tilde{\mu}_\alpha^{(n)} \delta^3(\mathbf{r} - \mathbf{R}_n) - \sum_n \frac{1}{3} \tilde{\Theta}_{\alpha\beta}^{(n)} \partial_\beta \delta^3(\mathbf{r} - \mathbf{R}_n) \quad (2.6)$$

$$\tilde{M}_\alpha \approx \sum_n \tilde{m}'_\alpha{}^{(n)} \delta^3(\mathbf{r} - \mathbf{R}_n) \quad (2.7)$$

with

$$\tilde{\mu}_\alpha^{(n)} \approx \alpha_{\alpha\beta}^{(n)} \tilde{E}_\beta^{(n)} - \frac{1}{\omega} \epsilon_{\delta\gamma\beta} G_{\alpha\delta}'^{(n)} \partial_\gamma \tilde{E}_\beta^{(n)} + \frac{1}{3} A_{\alpha,\beta\gamma}^{(n)} \partial_\gamma \tilde{E}_\beta^{(n)}, \quad (2.8)$$

$$\tilde{\Theta}_{\alpha\beta}^{(n)} \approx A_{\gamma,\alpha\beta}^{(n)} \tilde{E}_\gamma^{(n)} \quad (2.9)$$

$$\tilde{m}'_\alpha{}^{(n)} \approx i G_{\beta\alpha}'^{(n)} \tilde{E}_\beta^{(n)}, \quad (2.10)$$

where $\tilde{\mu}_\alpha^{(n)} = \tilde{\mu}_\alpha^{(n)}(t)$, $\tilde{\Theta}_{\alpha\beta}^{(n)} = \tilde{\Theta}_{\alpha\beta}^{(n)}(t)$ and $\tilde{m}'_\alpha{}^{(n)} = \tilde{m}'_\alpha{}^{(n)}(t)$ are the complex electric dipole, electric quadrupole and magnetic dipole moments of the n^{th} molecule and $\alpha_{\alpha\beta}^{(n)} = \alpha_{\beta\alpha}^{(n)} = \alpha_{\alpha\beta}^{(n)}(t)$, $G_{\alpha\beta}'^{(n)} = G_{\alpha\beta}'^{(n)}(t)$ and $A_{\alpha,\beta\gamma}^{(n)} = A_{\alpha,\gamma\beta}^{(n)} = A_{\alpha,\beta\gamma}^{(n)}(t)$ are the vibronic electric dipole-electric dipole, electric dipole-magnetic dipole and electric dipole-electric quadrupole polarisability tensors of the n^{th} molecule [28, 46]. The laboratory-fixed components of the polarisability tensors are related to the molecule-fixed components via relations like

$$\alpha_{\alpha\beta}^{(n)} = \ell_{\alpha\alpha'}^{(n)} \ell_{\beta\beta'}^{(n)} \alpha_{\alpha'\beta'}^{(n)}, \quad (2.11)$$

for example, where $\ell_{\alpha\alpha'}^{(n)} = \ell_{\alpha\alpha'}^{(n)}(\vartheta^{(n)}(t), \varphi^{(n)}(t), \chi^{(n)}(t))$ is the direction cosine tensor for

the n^{th} molecule [28, 105].

2.2.2 Incident light

We take the incident light (superscript i) to satisfy Maxwell's equations in the form

$$\nabla \cdot \tilde{\mathbf{D}}^i = 0, \quad (2.12)$$

$$\nabla \cdot \tilde{\mathbf{B}}^i = 0, \quad (2.13)$$

$$\nabla \times \tilde{\mathbf{E}}^i = -\frac{\partial \tilde{\mathbf{B}}^i}{\partial t} \quad (2.14)$$

$$\nabla \times \tilde{\mathbf{B}}^i = \mu_0 \frac{\partial \tilde{\mathbf{D}}^i}{\partial t} \quad (2.15)$$

together with the constitutive relation

$$\tilde{\mathbf{D}}^i \approx \epsilon \tilde{\mathbf{E}}^i - \gamma \nabla \times \tilde{\mathbf{E}}^i, \quad (2.16)$$

where $\tilde{\mathbf{D}}^i = \tilde{\mathbf{D}}^i(\mathbf{r}, t)$, $\tilde{\mathbf{E}}^i = \tilde{\mathbf{E}}^i(\mathbf{r}, t)$ and $\tilde{\mathbf{B}}^i = \tilde{\mathbf{B}}^i(\mathbf{r}, t)$ are the complex displacement, electric and magnetic fields of the incident light; ϵ is the average permittivity of the sample and γ is the average optical activity parameter of the sample [28, 46, 106]. The solutions of (2.12)-(2.16) are circularly polarised plane electromagnetic waves and superpositions thereof [28].

Let us assume that the incident light propagates only a short distance through the sample, as will typically be the case in an experiment using a small cuvette, for example. Accordingly, we neglect the optical rotation of the incident light ($\gamma \rightarrow 0$) and take

$$\tilde{\mathbf{E}}^i \approx E^{(0)} \tilde{\mathbf{e}}^i e^{i(\boldsymbol{\kappa}^i \cdot \mathbf{r} - \omega t)}, \quad (2.17)$$

$$\boldsymbol{\kappa}^i = \frac{\omega \mathbf{n}^i}{c} \quad (2.18)$$

$$\mathbf{n}^i = n \hat{\mathbf{z}} \quad (2.19)$$

with

$$\hat{\mathbf{e}}^H = \hat{\mathbf{y}}, \quad (2.20)$$

$$\hat{\mathbf{e}}^V = \hat{\mathbf{x}}, \quad (2.21)$$

$$\hat{\mathbf{e}}^L = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) \quad (2.22)$$

$$\hat{\mathbf{e}}^R = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} - i\hat{\mathbf{y}}), \quad (2.23)$$

where $E^{(0)}$, $\tilde{\mathbf{e}}^i$, $\boldsymbol{\kappa}^i$ and $\mathbf{n}^i$ are the electric-field amplitude, complex polarisation vector, wavevector and propagation vector of the incident light and $n = \sqrt{\epsilon/\epsilon_0}$ is the average refractive index of the sample with $\gamma = 0$.

2.2.3 Scattered light

We take the scattered light (superscript s) to be the difference between the total (no superscript) light and the incident light defined above, as

$$\tilde{\mathbf{D}}^s = \tilde{\mathbf{D}} - \tilde{\mathbf{D}}^i, \quad (2.24)$$

$$\tilde{\mathbf{E}}^s = \tilde{\mathbf{E}} - \tilde{\mathbf{E}}^i \quad (2.25)$$

$$\tilde{\mathbf{B}}^s = \tilde{\mathbf{B}} - \tilde{\mathbf{B}}^i, \quad (2.26)$$

where $\tilde{\mathbf{D}}^s = \tilde{\mathbf{D}}^s(\mathbf{r}, t)$, $\tilde{\mathbf{E}}^s = \tilde{\mathbf{E}}^s(\mathbf{r}, t)$ and $\tilde{\mathbf{B}}^s = \tilde{\mathbf{B}}^s(\mathbf{r}, t)$ are the complex displacement, electric and magnetic fields of the scattered light [72, 73].

Using (2.16), (2.24) and (2.25), we obtain

$$\tilde{\mathbf{D}}^s \approx \epsilon \tilde{\mathbf{E}}^s - \gamma \boldsymbol{\nabla} \times \tilde{\mathbf{E}}^s + \delta \tilde{\mathbf{D}} \quad (2.27)$$

with

$$\delta \tilde{\mathbf{D}} \approx \tilde{\mathbf{D}} - (\epsilon \tilde{\mathbf{E}} - \gamma \boldsymbol{\nabla} \times \tilde{\mathbf{E}}),$$

where $\delta \tilde{\mathbf{D}} = \delta \tilde{\mathbf{D}}(\mathbf{r}, t)$ embodies fluctuations with respect to the average optical prop-

erties of the sample, being the difference between the displacement field $\tilde{\mathbf{D}}$ and the form it would have if the sample had homogeneous and isotropic constitutive relations $(\epsilon\tilde{\mathbf{E}} - \gamma\nabla \times \tilde{\mathbf{E}})$.

Using (2.1)-(2.4), (2.12)-(2.15), (2.24)-(2.26) and (2.27) as well as the vector identity

$$\nabla \times (\nabla \times \tilde{\mathbf{D}}^s) = -\nabla^2 \tilde{\mathbf{D}}^s + \nabla(\nabla \cdot \tilde{\mathbf{D}}^s),$$

we find that $\tilde{\mathbf{D}}^s$ must satisfy the wave equation

$$\nabla^2 \tilde{\mathbf{D}}^s - \frac{n^2}{c^2} \frac{\partial^2 \tilde{\mathbf{D}}^s}{\partial t^2} + \mu_0 \gamma \frac{\partial^2 (\nabla \times \tilde{\mathbf{D}}^s)}{\partial t^2} \approx -\nabla \times (\nabla \times \delta \tilde{\mathbf{D}}), \quad (2.28)$$

which shows that the fluctuations embodied by the difference $\delta \tilde{\mathbf{D}}$ drive waves in the displacement $\tilde{\mathbf{D}}^s$ of the scattered light.

Neglecting multiple scattering, we take

$$\delta \tilde{\mathbf{D}} \approx \delta \tilde{\mathbf{D}}^i \quad (2.29)$$

with

$$\begin{aligned} \delta \tilde{D}_\alpha^i &= \epsilon_0 \tilde{E}_\alpha^i + \sum_n \alpha_{\alpha\beta}^{(n)} \delta^3(\mathbf{r} - \mathbf{R}_n) \tilde{E}_\beta^{i(n)} \\ &\quad - \sum_n \left(\frac{1}{\omega} \epsilon_{\delta\gamma\beta} G'_{\alpha\delta}{}^{(n)} - \frac{1}{3} A_{\alpha,\beta\gamma}^{(n)} \right) \delta^3(\mathbf{r} - \mathbf{R}_n) \partial_\gamma \tilde{E}_\beta^{i(n)} \\ &\quad + \sum_n \left(\frac{1}{\omega} \epsilon_{\delta\gamma\alpha} G'_{\beta\delta}{}^{(n)} - \frac{1}{3} A_{\beta,\alpha\gamma}^{(n)} \right) \partial_\gamma \delta^3(\mathbf{r} - \mathbf{R}_n) \tilde{E}_\beta^{i(n)} \\ &\quad - (\epsilon \tilde{E}_\alpha^i + \gamma \epsilon_{\alpha\beta\gamma} \partial_\gamma \tilde{E}_\beta^i), \end{aligned} \quad (2.30)$$

where $\delta \tilde{\mathbf{D}}^i = \delta \tilde{\mathbf{D}}^i(\mathbf{r}, t)$ embodies fluctuations coupled directly to the incident light. The single-scattering condition $4\pi\mu_0^2\omega^4\alpha^2NV^{1/3} \ll 1$ should be well satisfied in the visible domain by typical small-molecule liquids for a cuvette of volume $V = 1 \text{ cm}^3$, say.

Let us assume that the scattered light (like the incident light) propagates only a short distance through the sample. Accordingly, we neglect the optical rotation of the

scattered light ($\gamma = 0$) and take the solution of (2.28) with (2.29) to be

$$\tilde{\mathbf{D}}^s \approx \frac{1}{4\pi} \nabla \times \left\{ \nabla \times \left[\iiint_V \frac{\delta \tilde{\mathbf{D}}^i(\mathbf{r}', t')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \right] \right\}, \quad (2.31)$$

where $t' = t - n|\mathbf{r} - \mathbf{r}'|/c$ is the delayed time [28, 106]. Let us assume moreover that the fluctuations are slow relative to the angular frequency ω of the incident light. Accordingly, we simplify (2.31) by taking

$$\tilde{\mathbf{D}}^s \approx \frac{1}{4\pi} \nabla \times \left\{ \nabla \times \left[\iiint_V \frac{\delta \tilde{\mathbf{D}}^i(\mathbf{r}', t) e^{i\omega t} e^{-i\omega t'}}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \right] \right\}, \quad (2.32)$$

where we have effectively separated the fast and slow time dependencies of $\delta \tilde{\mathbf{D}}^i$ by writing

$$\delta \tilde{\mathbf{D}}^i(\mathbf{r}', t') = [\delta \tilde{\mathbf{D}}^i(\mathbf{r}', t') \exp(i\omega t')] \exp(-i\omega t') \rightarrow [\delta \tilde{\mathbf{D}}^i(\mathbf{r}', t) \exp(i\omega t)] \exp(-i\omega t'),$$

thus retaining delay for the fast dependencies only [72, 73].

2.2.4 Analysed signal at the detector

Let us focus now on the form of the scattered light at the detector (superscript d). We take the y - z plane to be the scattering plane, without loss of generality. It is convenient to introduce unit vectors

$$\hat{\mathbf{x}}^d = \hat{\mathbf{x}}, \quad (2.33)$$

$$\hat{\mathbf{y}}^d = \cos \xi \hat{\mathbf{y}} - \sin \xi \hat{\mathbf{z}} \quad (2.34)$$

$$\hat{\mathbf{z}}^d = \sin \xi \hat{\mathbf{y}} + \cos \xi \hat{\mathbf{z}} \quad (2.35)$$

aligned with the detector, where ξ is the scattering angle.

As the detector lies in the far field, we take

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{1}{R} \quad (2.36)$$

$$\omega t' \approx \omega t - \kappa R + \boldsymbol{\kappa}^{\text{d}} \cdot \mathbf{r}' \quad (2.37)$$

with

$$\kappa = \frac{\omega n}{c}, \quad (2.38)$$

$$\boldsymbol{\kappa}^{\text{d}} = \frac{\omega \mathbf{n}^{\text{d}}}{c} \quad (2.39)$$

$$\mathbf{n}^{\text{d}} = n \hat{\mathbf{z}}^{\text{d}}, \quad (2.40)$$

where R is the distance from the centre of the scattering volume V to the detector ($R \gg V^{1/3}$, $\kappa R \gg 1$) and κ , $\boldsymbol{\kappa}^{\text{d}}$ and $\mathbf{n}^{\text{d}}$ are the angular wavenumber, wavevector and propagation vector of the scattered light at the detector [28, 106]. Using (2.32), (2.36) and (2.37) as well as the vector identity

$$-\boldsymbol{\kappa}^{\text{d}} \times (\boldsymbol{\kappa}^{\text{d}} \times \mathbf{V}) = (\boldsymbol{\kappa}^{\text{d}} \cdot \boldsymbol{\kappa}^{\text{d}}) \mathbf{V} - \boldsymbol{\kappa}^{\text{d}} (\boldsymbol{\kappa}^{\text{d}} \cdot \mathbf{V})$$

whilst retaining only the leading contributions which fall off as $1/R$, we find that the complex electric field $\tilde{\mathbf{E}}^{\text{di}} = \tilde{\mathbf{E}}^{\text{di}}(t)$ of the scattered light at the detector has the form

$$\tilde{E}_{\alpha}^{\text{di}} \approx \frac{\mu_0 \omega^2}{4\pi R} e^{i(\kappa R - \omega t)} (\delta_{\alpha\beta} - \hat{n}_{\alpha}^{\text{d}} \hat{n}_{\beta}^{\text{d}}) \iiint_V \delta \tilde{D}_{\beta}^{\text{i}}(\mathbf{r}', t) e^{i\omega t} e^{-i\boldsymbol{\kappa}^{\text{d}} \cdot \mathbf{r}'} d^3 \mathbf{r}', \quad (2.41)$$

where we have taken $\tilde{\mathbf{E}}^{\text{di}} \approx \tilde{\mathbf{D}}^{\text{di}}/\epsilon$, $\tilde{\mathbf{D}}^{\text{di}} = \tilde{\mathbf{D}}^{\text{di}}(t)$ being the complex displacement of the scattered light at the detector. Substituting (2.30) explicitly into (2.41) then integrating by parts and neglecting boundary terms as well as forward-scattering contributions, we

obtain

$$\begin{aligned} \tilde{E}_\alpha^{\text{di}} \approx & \frac{\mu_0 \omega^2 E^{(0)}}{4\pi R} e^{i(\kappa R - \omega t)} (\delta_{\alpha\beta} - \hat{n}_\alpha^{\text{d}} \hat{n}_\beta^{\text{d}}) \left[\tilde{\alpha}_{\beta\gamma} \tilde{e}_\gamma^{\text{i}} - \frac{\text{i}}{c} (\tilde{G}'_{\beta\epsilon} \epsilon_{\epsilon\delta\gamma} \tilde{e}_\gamma^{\text{i}} n_\delta^{\text{i}} - \tilde{G}'_{\gamma\epsilon} \epsilon_{\epsilon\delta\beta} \tilde{e}_\gamma^{\text{i}} n_\delta^{\text{d}}) \right. \\ & \left. + \frac{\text{i}\omega}{3c} (\tilde{A}_{\beta,\gamma\delta} \tilde{e}_\gamma^{\text{i}} n_\delta^{\text{i}} - \tilde{A}_{\gamma,\beta\delta} \tilde{e}_\gamma^{\text{i}} n_\delta^{\text{d}}) \right] \end{aligned} \quad (2.42)$$

with

$$\tilde{\alpha}_{\alpha\beta} = \sum_n \alpha_{\alpha\beta}^{(n)} e^{-\text{i}\mathbf{q} \cdot \mathbf{R}_n}, \quad (2.43)$$

$$\tilde{G}'_{\alpha\beta} = \sum_n G'_{\alpha\beta}^{(n)} e^{-\text{i}\mathbf{q} \cdot \mathbf{R}_n} \quad (2.44)$$

$$\tilde{A}_{\alpha,\beta\gamma} = \sum_n A_{\alpha,\beta\gamma}^{(n)} e^{-\text{i}\mathbf{q} \cdot \mathbf{R}_n}, \quad (2.45)$$

where $\tilde{\alpha}_{\alpha\beta} = \tilde{\alpha}_{\alpha\beta}(t)$, $\tilde{G}'_{\alpha\beta} = \tilde{G}'_{\alpha\beta}(t)$ and $\tilde{A}_{\alpha,\beta\gamma} = \tilde{A}_{\alpha,\beta\gamma}(t)$ are spatial Fourier transforms of polarisability densities, evaluated at the non-zero wavevector difference [72, 73]

$$\mathbf{q} = \boldsymbol{\kappa}^{\text{d}} - \boldsymbol{\kappa}^{\text{i}}. \quad (2.46)$$

Note that $q = |\mathbf{q}| = 2\omega n \sin(\xi/2)/c$.

We take the analysed signal $\tilde{A}^{\text{di}} = \tilde{A}^{\text{di}}(t)$ at the detector to be

$$\tilde{A}^{\text{di}} = \tilde{a}_\alpha^{\text{d}*} \tilde{E}_\alpha^{\text{di}} \quad (2.47)$$

with

$$\hat{\mathbf{a}}^{\text{H}} = \hat{\mathbf{y}}^{\text{s}}, \quad (2.48)$$

$$\hat{\mathbf{a}}^{\text{V}} = \hat{\mathbf{x}}^{\text{s}}, \quad (2.49)$$

$$\tilde{\mathbf{a}}^{\text{L}} = \frac{1}{\sqrt{2}} (\hat{\mathbf{x}}^{\text{s}} + \text{i}\hat{\mathbf{y}}^{\text{s}}) \quad (2.50)$$

$$\tilde{\mathbf{a}}^{\text{R}} = \frac{1}{\sqrt{2}} (\hat{\mathbf{x}}^{\text{s}} - \text{i}\hat{\mathbf{y}}^{\text{s}}), \quad (2.51)$$

where $\tilde{\mathbf{a}}^{\text{d}}$ is an analysis vector that picks off the desired polarisation component of the electric field $\tilde{\mathbf{E}}^{\text{di}}$.

2.2.5 Frequency spectrum and total intensity

The frequency spectrum $\mathbb{I}^{\text{di}} = \mathbb{I}^{\text{di}}(\Omega)$ of the analysed signal $\tilde{A}^{\text{di}}$ can be calculated as the temporal Fourier transform of the autocorrelation of $\tilde{A}^{\text{di}}$, as

$$\mathbb{I}^{\text{di}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \tilde{A}^{\text{di}*}(t) \tilde{A}^{\text{di}}(t + \tau) \rangle e^{i\Omega\tau} d\tau, \quad (2.52)$$

where the angular brackets denote a time average, Ω is an angular frequency and τ is a correlation time [73]. The total intensity I^{di} of the analysed signal can then be calculated as the integral of the frequency spectrum $\mathbb{I}^{\text{di}}$, as

$$I^{\text{di}} = \int_{-\infty}^{\infty} \mathbb{I}^{\text{di}}(\Omega) d\Omega. \quad (2.53)$$

Note that $\mathbb{I}^{\text{di}} = 0$ for $\Omega < 0$, assuming that $\tilde{A}^{\text{di}} = 0$ for $\Omega < 0$.

Substituting (2.42) and (2.47) into (2.52) whilst working to first order in multipolar expansions, we obtain

$$\begin{aligned} \mathbb{I}^{\text{di}} \approx & \frac{30K}{2\pi} \int_{-\infty}^{\infty} \langle \tilde{\alpha}^{\text{di}*}(t) \tilde{\alpha}^{\text{di}}(t + \tau) \\ & + \tilde{\alpha}^{\text{di}*}(t) \tilde{\chi}^{\text{di}}(t + \tau) + \tilde{\alpha}^{\text{di}}(t + \tau) \tilde{\chi}^{\text{di}*}(t) \rangle e^{i(\Omega - \omega)\tau} d\tau \end{aligned} \quad (2.54)$$

with

$$K = \frac{1}{30} \left(\frac{\mu_0 \omega^2 E^{(0)}}{4\pi R} \right)^2, \quad (2.55)$$

$$\tilde{\alpha}^{\text{di}} = \tilde{\alpha}_{\alpha}^{\text{d}*} \tilde{\alpha}_{\alpha\beta} \tilde{e}_{\beta}^{\text{i}} \quad (2.56)$$

$$\begin{aligned} \tilde{\chi}^{\text{di}} = & -\frac{\text{i}}{c} (\tilde{\alpha}_{\alpha}^{\text{d}*} \tilde{G}'_{\alpha\delta} \epsilon_{\delta\gamma\beta} \tilde{e}_{\beta}^{\text{i}} n_{\gamma}^{\text{i}} - \tilde{\alpha}_{\alpha}^{\text{d}*} \tilde{G}'_{\beta\delta} \epsilon_{\delta\gamma\alpha} \tilde{e}_{\beta}^{\text{i}} n_{\gamma}^{\text{s}}) \\ & + \frac{\text{i}\omega}{3c} (\tilde{\alpha}_{\alpha}^{\text{d}*} \tilde{A}_{\alpha,\beta\gamma} \tilde{e}_{\beta}^{\text{i}} n_{\gamma}^{\text{i}} - \tilde{\alpha}_{\alpha}^{\text{d}*} \tilde{A}_{\beta,\alpha\gamma} \tilde{e}_{\beta}^{\text{i}} n_{\gamma}^{\text{s}}), \end{aligned} \quad (2.57)$$

a	b	c	d	$3c\mathbb{A}/nK$	$3c\mathbb{B}/nK$	$3c\mathbb{C}/nK$
R	H	L	H	$24\beta_G^2 - 8\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
R	V	L	V	$180\alpha G' + 28\beta_G^2 + 4\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	0
R	N	L	N	$90\alpha G' + 26\beta_G^2 - 2\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$90\alpha G' + 2\beta_G^2 + 6\beta_A^2$
H	R	H	L	$24\beta_G^2 - 8\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
V	R	V	L	$180\alpha G' + 28\beta_G^2 + 4\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	0
N	R	N	R	$90\alpha G' + 26\beta_G^2 - 2\beta_A^2$	$180\alpha G' - 20\beta_G^2 - 12\beta_A^2$	$90\alpha G' + 2\beta_G^2 + 6\beta_A^2$
R	R	L	L	$180\alpha G' + 52\beta_G^2 - 4\beta_A^2$	$360\alpha G' - 40\beta_G^2 - 24\beta_A^2$	$180\alpha G' + 4\beta_G^2 + 12\beta_A^2$
a	b	c	d	$3\mathbb{D}/K$	$3\mathbb{E}/K$	$3\mathbb{F}/K$
R	H	L	H	$12\beta^2$	0	$90\alpha^2 + 2\beta^2$
R	V	L	V	$90\alpha^2 + 14\beta^2$	0	0
R	N	L	N	$45\alpha^2 + 13\beta^2$	0	$45\alpha^2 + \beta^2$
H	R	H	L	$12\beta^2$	0	$90\alpha^2 + 2\beta^2$
V	R	V	L	$90\alpha^2 + 14\beta^2$	0	0
N	R	N	R	$45\alpha^2 + 13\beta^2$	0	$45\alpha^2 + \beta^2$
R	R	L	L	$45\alpha^2 + 13\beta^2$	$90\alpha^2 - 10\beta^2$	$45\alpha^2 + \beta^2$

Table 2.1: Circular spectral differential coefficients for some important SCP, ICP and DCP_I configurations. The N results are averages of the relevant H and V results, the N standing for “natural” (unpolarised incident light or unanalysed scattered light). Note that the entries in rows one through three and eight through eleven match the entries in rows four through six and twelve through fourteen respectively, in accord with the principle of reciprocity [28, 50–52].

where K is a prefactor that contains the usual ω^4 , $E^{(0)2}$ and $1/R^2$ scalings characteristic of Rayleigh scattering in the far field and $\tilde{\alpha}^{\text{di}} = \tilde{\alpha}^{\text{di}}(t)$ and $\tilde{\chi}^{\text{di}} = \tilde{\chi}^{\text{di}}(t)$ are convenient shorthands.

2.2.6 Dimensionless circular spectral and intensity differentials

RayOA (and by extension RayBOA) can manifest as an intensity difference with respect to left- and right-handed circular polarisation states in the scattered light (scattered circular polarisation or SCP) [1], the incident light (incident circular polarisation or ICP) [2] or both simultaneously (dual circular polarisation or DCP_I) [48].

As convenient measures of RayBOA, we identify dimensionless circular spectral differentials $\Delta = \Delta(\Omega)$ of the form

$$\begin{aligned}
 \Delta &= \frac{\mathbb{I}^{\text{ab}} - \mathbb{I}^{\text{cd}}}{\mathbb{I}^{\text{ab}} + \mathbb{I}^{\text{cd}}} \\
 &\approx \frac{\mathbb{A} + \mathbb{B} \cos \xi + \mathbb{C} \cos^2 \xi}{\mathbb{D} + \mathbb{E} \cos \xi + \mathbb{F} \cos^2 \xi}
 \end{aligned} \tag{2.58}$$

and circular intensity differentials Δ of the form

$$\Delta = \frac{I^{ab} - I^{cd}}{I^{ab} + I^{cd}} \approx \frac{\int_{-\infty}^{\infty} \mathbb{A}(\Omega) d\Omega + \int_{-\infty}^{\infty} \mathbb{B}(\Omega) d\Omega \cos \xi + \int_{-\infty}^{\infty} \mathbb{C}(\Omega) d\Omega \cos^2 \xi}{\int_{-\infty}^{\infty} \mathbb{D}(\Omega) d\Omega + \int_{-\infty}^{\infty} \mathbb{E}(\Omega) d\Omega \cos \xi + \int_{-\infty}^{\infty} \mathbb{F}(\Omega) d\Omega \cos^2 \xi}, \quad (2.59)$$

where a and c refer to analysed polarisation states of the scattered light, b and d refer to polarisation states of the incident light and $\mathbb{A} = \mathbb{A}(\Omega)$, $\mathbb{B} = \mathbb{B}(\Omega)$, $\mathbb{C} = \mathbb{C}(\Omega)$, $\mathbb{D} = \mathbb{D}(\Omega)$, $\mathbb{E} = \mathbb{E}(\Omega)$ and $\mathbb{F} = \mathbb{F}(\Omega)$ are coefficients that depend on the specific configuration being considered. Substituting (2.54) into (2.58) and (2.59) and making use of basic symmetry arguments, we obtain the results listed in Table 2.1 with

$$\alpha^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \frac{1}{9} \tilde{\alpha}_{\alpha\alpha}^*(t) \tilde{\alpha}_{\beta\beta}(t + \tau) \right\rangle e^{i(\Omega - \omega)\tau} d\tau, \quad (2.60)$$

$$\beta^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \frac{1}{2} [3\tilde{\alpha}_{\alpha\beta}^*(t) \tilde{\alpha}_{\alpha\beta}(t + \tau) - \tilde{\alpha}_{\alpha\alpha}^*(t) \tilde{\alpha}_{\beta\beta}(t + \tau)] \right\rangle e^{i(\Omega - \omega)\tau} d\tau, \quad (2.61)$$

$$\alpha\mathbb{G}' = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \frac{1}{18} [\tilde{\alpha}_{\alpha\alpha}^*(t) \tilde{G}'_{\beta\beta}(t + \tau) + \tilde{\alpha}_{\alpha\alpha}(t + \tau) \tilde{G}'_{\beta\beta}^*(t)] \right\rangle e^{i(\Omega - \omega)\tau} d\tau, \quad (2.62)$$

$$\begin{aligned} \beta_G^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \frac{1}{4} [3\tilde{\alpha}_{\alpha\beta}^*(t) \tilde{G}'_{\alpha\beta}(t + \tau) - \tilde{\alpha}_{\alpha\alpha}^*(t) \tilde{G}'_{\beta\beta}(t + \tau) \right. \\ \left. + 3\tilde{\alpha}_{\alpha\beta}(t + \tau) \tilde{G}'_{\alpha\beta}^*(t) - \tilde{\alpha}_{\alpha\alpha}(t + \tau) \tilde{G}'_{\beta\beta}^*(t)] \right\rangle e^{i(\Omega - \omega)\tau} d\tau \end{aligned} \quad (2.63)$$

$$\beta_A^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \frac{\omega}{4} [\epsilon_{\alpha\beta\gamma} \tilde{\alpha}_{\alpha\delta}^*(t) \tilde{A}_{\beta,\gamma\delta}(t + \tau) + \epsilon_{\alpha\beta\gamma} \tilde{\alpha}_{\alpha\delta}(t + \tau) \tilde{A}_{\beta,\gamma\delta}^*(t)] \right\rangle e^{i(\Omega - \omega)\tau} d\tau, \quad (2.64)$$

where $\alpha^2 = \alpha^2(\Omega)$ accounts for isotropic electric dipole-electric dipole scattering, $\beta^2 = \beta^2(\Omega)$ accounts for anisotropic electric dipole-electric dipole scattering, $\alpha\mathbb{G}' = \alpha\mathbb{G}'(\Omega)$ accounts for isotropic electric dipole-magnetic dipole scattering, $\beta_G^2 = \beta_G^2(\Omega)$ accounts for anisotropic electric dipole-magnetic dipole scattering and $\beta_A^2 = \beta_A^2(\Omega)$ accounts for anisotropic electric dipole-electric quadrupole scattering. Note that α^2 and β^2 are chirally insensitive whereas $\alpha\mathbb{G}'$, β_G^2 and β_A^2 have equal magnitudes but opposite signs for enantiomorphic samples. It follows that both Δ and Δ have equal magnitudes but opposite signs for enantiomorphous samples, thus serving as signatures of chirality.

Let us emphasise here that the circular differentials Δ and Δ are not simply related

to each other, in particular that

$$\Delta \neq \int_{-\infty}^{\infty} \Delta(\Omega) d\Omega. \quad (2.65)$$

They provide different insights, as we will see below.

As a quick check on the validity of our results, we note that for the special case of a single molecule held fixed at the origin, we have $\alpha^2 \rightarrow \alpha^2 \delta(\Omega - \omega)$, $\beta^2 \rightarrow \beta^2 \delta(\Omega - \omega)$, $\alpha G' \rightarrow \alpha G' \delta(\Omega - \omega)$, $\beta_G^2 \rightarrow \beta_G^2 \delta(\Omega - \omega)$ and $\beta_A^2 \rightarrow \beta_A^2 \delta(\Omega - \omega)$, where α^2 , β^2 , $\alpha G'$, β_G^2 and β_A^2 are the usual single-molecule invariants [14, 28]. This sees our results for the circular intensity differentials Δ reduce immediately to the (rotationally averaged) results reported previously elsewhere [2, 14, 28, 66], as they should.

2.3 Toy model

For the sake of illustration, let us now evaluate the circular differentials Δ and Δ for a toy model of an enantiopure neat liquid. This model is not meant to provide accurate predictions for real liquids. Rather, we include it to demonstrate the mathematical extraction of spectra.

Considering molecules with quasi-cylindrical symmetry for the sake of simplicity, we take

$$\alpha_{\alpha\beta}^{(n)} = \alpha \delta_{\alpha\beta} + \Delta\alpha \left(\hat{u}_{\alpha}^{(n)} \hat{u}_{\beta}^{(n)} - \frac{1}{3} \delta_{\alpha\beta} \right), \quad (2.66)$$

$$G'_{\alpha\beta}^{(n)} = G' \delta_{\alpha\beta} + \Delta G' \left(\hat{u}_{\alpha}^{(n)} \hat{u}_{\beta}^{(n)} - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (2.67)$$

$$\begin{aligned} A_{\alpha\beta}^{(n)} &= \frac{\omega}{2} \epsilon_{\alpha\gamma\delta} A_{\gamma,\beta\delta}^{(n)} \\ &= \Delta A \left(\hat{u}_{\alpha}^{(n)} \hat{u}_{\beta}^{(n)} - \frac{1}{3} \delta_{\alpha\beta} \right), \end{aligned} \quad (2.68)$$

where α and G' are isotropic polarisabilities; $\Delta\alpha$, $\Delta G'$ and ΔA are polarisability anisotropies and $\hat{\mathbf{u}}^{(n)} = \hat{\mathbf{u}}^{(n)}(t)$ is a unit vector dictated by the orientation of the n^{th} molecule [28, 73]. Note that $\Delta\alpha = \Delta G' = \Delta A = 0$ for molecules with spherical

rather than quasi-cylindrical symmetry. Substituting (2.66)-(2.68) into (2.60)-(2.64), we obtain

$$\alpha^2 = \alpha^2 S, \quad (2.69)$$

$$\beta^2 = \beta^2 \Theta, \quad (2.70)$$

$$\alpha G' = \alpha G' S, \quad (2.71)$$

$$\beta_G^2 = \beta_G^2 \Theta \quad (2.72)$$

$$\beta_A^2 = \beta_A^2 \Theta \quad (2.73)$$

with

$$S = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \sum_n \sum_m e^{i\mathbf{q} \cdot [\mathbf{R}_n(t) - \mathbf{R}_m(t+\tau)]} \rangle e^{i(\Omega - \omega)\tau} d\tau \quad (2.74)$$

$$\begin{aligned} \Theta = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \sum_n \sum_m \frac{1}{2} \{ 3[\hat{\mathbf{u}}^{(n)}(t) \cdot \hat{\mathbf{u}}^{(m)}(t+\tau)]^2 \\ - 1 \} e^{i\mathbf{q} \cdot [\mathbf{R}_n(t) - \mathbf{R}_m(t+\tau)]} \rangle e^{i(\Omega - \omega)\tau} d\tau, \end{aligned} \quad (2.75)$$

where α^2 , β^2 , $\alpha G'$, $\beta^2 = \Delta \alpha^2$, $\beta_G^2 = \Delta \alpha \Delta G'$ and $\beta_A^2 = 2\Delta \alpha \Delta A/3$ are the usual single-molecule invariants [14, 28] and $S = S(\Omega)$ and $\Theta = \Theta(\Omega)$ are dynamic structure factors [73, 107].

A simple hydrodynamic model (neglecting intramolecular relaxation) gives

$$\begin{aligned} S \approx N^2 V \chi_T k_B T \left\{ \left(1 - \frac{1}{\gamma} \right) \frac{1}{\pi} \frac{D_T q^2}{(\Omega - \omega)^2 + (D_T q^2)^2} \right. \\ \left. + \frac{1}{2\gamma} \left[\frac{1}{\pi} \frac{\Gamma q^2}{(\Omega - \omega + vq)^2 + (\Gamma q^2)^2} + \frac{1}{\pi} \frac{\Gamma q^2}{(\Omega - \omega - vq)^2 + (\Gamma q^2)^2} \right] \right\}, \end{aligned} \quad (2.76)$$

where N is the average number density, χ_T is the isothermal compressibility, T is the temperature, γ is the heat capacity ratio, D_T is the thermal diffusivity, v is the adiabatic speed of sound and Γ is the classical sound attenuation coefficient [72, 73, 75, 100].

A simple rotational diffusion model (neglecting translational effects and orientational

correlations between molecules) gives

$$\Theta \approx NV \frac{1}{\pi} \frac{\Gamma_{\Theta}}{(\Omega - \omega)^2 + \Gamma_{\Theta}^2}, \quad (2.77)$$

where Γ_{Θ} is a tumbling rate [73, 108]. The time-domain molecular dynamics that underpin these forms for S and Θ are described explicitly in [72, 73, 75, 100, 108].

Focussing on a right-angled SCP configuration with vertically polarised incident light for the sake of concreteness, we have

$$\Delta = \frac{\frac{nK}{3c}(180\alpha G'^S + 28\beta_G^2\Theta + 4\beta_A^2\Theta)}{\frac{K}{3}(90\alpha^2S + 14\beta^2\Theta)}, \quad (2.78)$$

$$\Delta = \frac{\frac{nK}{3c}NV(N\chi_T k_B T 180\alpha G' + 28\beta_G^2 + 4\beta_A^2)}{\frac{K}{3}NV(N\chi_T k_B T 90\alpha^2 + 14\beta^2)}. \quad (2.79)$$

Note that the circular intensity differential Δ here reduces to the previously reported result [2, 14, 28, 66] when $N\chi_T k_B T = 1$ (as in an ideal gas). For a liquid with $N\chi_T k_B T < 1$, the isotropic ($\alpha^2, \alpha G'$) contributions to Δ are suppressed relative to the anisotropic ($\beta^2, \beta_G^2, \beta_A^2$) contributions, changing the magnitude of Δ and perhaps even the sign; a demonstration of the need for our extended theory. The circular spectral differential Δ offers more information than Δ in that the isotropic and anisotropic contributions can be distinguished as a function of the angular frequency Ω . In the limiting case where $\Gamma_{\Theta} \gg vq \gg \Gamma q^2 > D_T q^2$, we find in particular that

$$\Delta(\omega) \approx \Delta(\omega \mp vq) \approx \frac{\frac{nK}{3c}180\alpha G'}{\frac{K}{3}90\alpha^2} \lim_{|\Omega - \omega| \gg vq} \Delta \approx \frac{\frac{nK}{3c}(28\beta_G^2 + 4\beta_A^2)}{\frac{K}{3}14\beta^2}.$$

Using typical values [14], this leads us to predict that

$$|\Delta(\omega)| \approx |\Delta(\omega \mp vq)| \sim 10^{-4} - 10^{-5} \quad \lim_{|\Omega - \omega| \gg vq} |\Delta| \sim 10^{-3} - 10^{-4},$$

although considerable variation is possible, of course.

These features are illustrated in Fig. 2.2 for $\omega = 3.54 \text{ Prad s}^{-1}$, $n = 1.40$, $\gamma = 1.33$, $N\chi_T k_B T = 0.100$, $D_T q^2 / 2\pi = 80.0 \text{ MHz}$, $vq / 2\pi = 3.00 \text{ GHz}$, $\Gamma q^2 / 2\pi = 160 \text{ MHz}$,

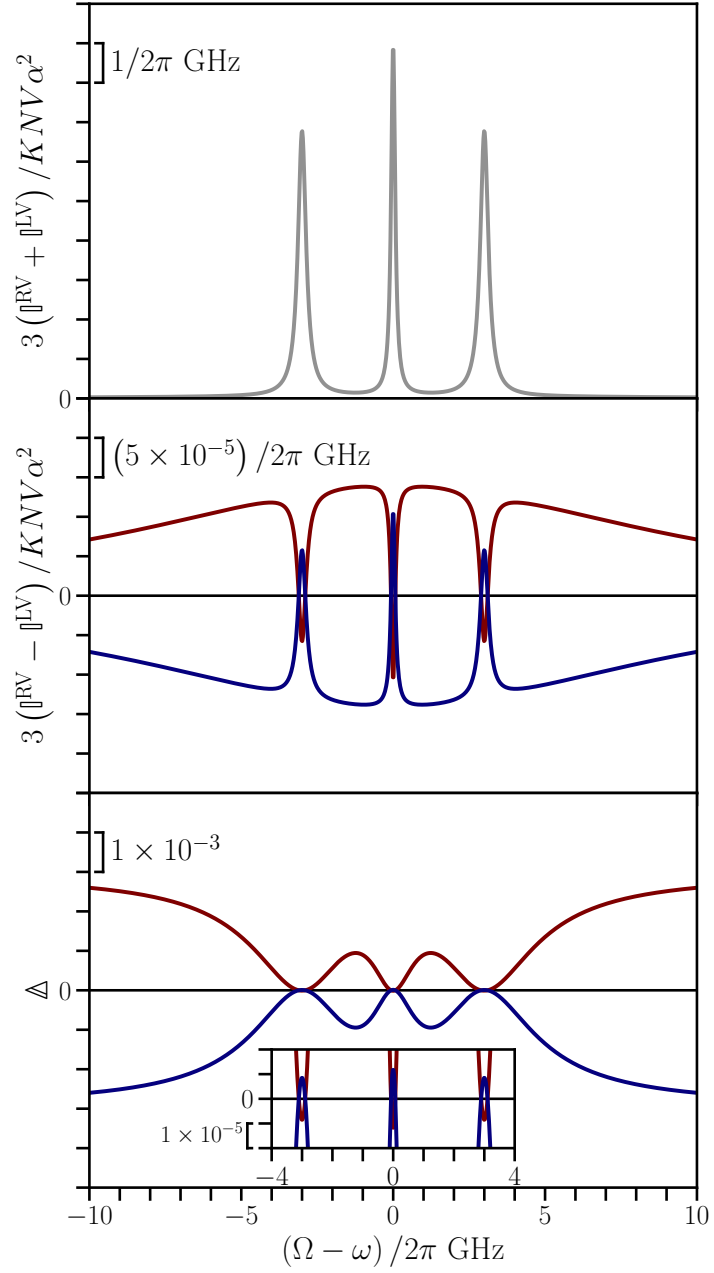


Figure 2.2: Circular spectra predicted for a toy model of an enantiopure neat liquid. The red and blue curves correspond to opposite enantiomers.

$\Gamma_{\Theta}/2\pi = 10.0 \text{ GHz}$, $\beta^2 = 0.100\alpha^2$, $\alpha G'/c = \mp 1.00 \times 10^{-5}\alpha^2$ and $\beta_G^2/c = \beta_A^2/c = \pm 1.00 \times 10^{-4}\alpha^2$, where the upper and lower signs correspond to opposite enantiomers. The circular spectral sum $\ell^{\text{RV}} + \ell^{\text{LV}}$ (i.e. the spectrum of the S_0 Stokes parameter of the

scattered light [28]) is positive and consists of a narrow Gross (centre) line [99, 100] and narrow Brillouin lines [86, 91, 92, 99] superposed with a broad Rayleigh wing [93–98]. The circular spectral difference $\mathbb{I}^{\text{RV}} - \mathbb{I}^{\text{LV}}$ (i.e. the spectrum of the S_3 Stokes parameter of the scattered light [28]) has opposite signs for opposite enantiomers, appearing inverted at the Gross and Brillouin lines as we have taken $180\alpha G'$ and $28\beta_G^2 + 4\beta_A^2$ to have opposite relative signs. The resulting circular spectral differential Δ also has opposite signs for opposite enantiomers and appears inverted at the Gross and Brillouin lines, where it is suppressed in magnitude in accord with our prediction above.

2.4 Summary and outlook

In this chapter, we have presented a theory of RayBOA applicable to dense samples such as neat liquids. There are many possible avenues for future research.

We have evaluated the circular differentials for a toy model of an enantiopure neat liquid. It remains for us to consider more realistic models for a variety of different samples. Molecular dynamics simulations have recently been applied with success to ROA [77, 109, 110] and might be developed for RayBOA as well.

We have adopted a microscopic approach, facilitating comparison with the existing theory of RayOA [1, 2, 14, 28, 46, 66–71]. A macroscopic approach is also possible [72, 73, 75, 83, 85] and might yield new insights. Care will need to be taken with the choice of macroscopic constitutive relations [111, 112], which must include electric dipole-electric quadrupole contributions to describe RayBOA correctly even for isotropic samples.

We have focussed on SCP, ICP and DCP_I RayBOA for off-resonant illumination of a fluid by planar light. Interesting new features should emerge for illumination near resonance [48, 67, 113, 114], anisotropic samples [67] and illumination by structured light [68, 70, 71, 115]. It should also prove fruitful to consider the influence of static magnetic fields, static electric fields and higher-order multipolar contributions, which can give rise to related effects such as magnetic Rayleigh optical activity [116], electric Rayleigh optical activity [58, 117], circular intensity differential scattering [55] and second-order

linear light scattering [69].

A particularly interesting question is whether Rayleigh-Brillouin optical activity can be used to detect chiral (acoustic) phonons in appropriate samples [77, 118–120].

Although our focus in this chapter has been on small molecules, similar ideas can be developed for larger scatterers, including large biomolecules [54–58].

Chapter 3

Strategy for First Measurements

3.1 Introduction

Prior to this PhD, measurements of RayOA had never been reported for small chiral molecules [28]. A major aim of this work was to rectify this omission and introduce RayOA as a new chiroptical tool. To this end, we designed and constructed a dedicated RayOA instrument (described in chapter 4) and used it to take the first-ever measurements of RayOA for small chiral molecules (described in chapter 5) [121]. In this short chapter, we preface the above by motivating our choice of wavelength, scattering angle and polarisation configuration for the instrument as well as our choice of small chiral molecule for first measurements. Included are quantum chemical predictions of Rayleigh scattering invariants, RayOA invariants and the resulting circular intensity differentials.

3.2 Choice of laser wavelength, scattering angle and polarisation configuration

3.2.1 Laser wavelength

Rayleigh scattering scales with wavelength far off resonance as $1/\lambda^4$ to good approximation and RayOA scales as $1/\lambda^5$, meaning the circular intensity differential Δ scales as $1/\lambda$. The incentive then was to choose a small laser wavelength to maximise the

intensity of scattered light as well as the magnitude of Δ . At the same time, we wanted to avoid potential confusion with fluorescence and other resonant effects. Ultimately, we chose to work at a laser wavelength of $\lambda = 532\text{ nm}$ on the basis that this should provide adequate scattered intensity whilst sitting comfortably in a window of transparency for many small chiral molecules, being below electronic resonances and above vibrational resonances. This is a frequently used laser wavelength so high quality, stable, narrow-linewidth lasers were readily available as were high quality optical components such as high extinction ratio linear polarisers and wave plates. In addition, the silicon based sensors used in most CCD and sCMOS cameras have spectral quantum efficiencies that peak around 532 nm , facilitating efficient detection. Similarly for the spectral detection efficiency of the human eye, which helped with the assembly of the instrument when aligning optical components with the aid of faint reflected spots for example.

3.2.2 Scattering angle

In terms of scattering angle, we chose to deploy our detection train at right angles ($\xi = 90^\circ$) relative to the incident beam. Backscattering ($\xi = 180^\circ$) is popular in ROA but is undesirable for RayOA as it would be difficult to distinguish the scattered light from the retro-reflected incident laser beam due to their quasi-degenerate frequencies. For similar reasons, forward or near-forward scattering ($\xi \approx 0^\circ$) is undesirable in the case of RayOA as there would be confusion between transmitted and scattered light. We therefore deemed a 90° scattering angle coupled with an appropriate choice of polarisation configuration (which will be further explored below) to be the optimal choice.

3.2.3 Polarisation configuration

As mentioned briefly in chapter 1, there are three main polarisation configurations in RayOA, namely ICP, SCP and DCP. DCP is the most complex to implement as it requires modulation both on the incident and scattered light. It is also better suited to ROA than RayOA as there is no frequency degeneracy of the scattered and incident light in the former. A major advantage of the SCP configuration using horizontally polarised

incident light and a $\xi = 90^\circ$ scattering angle is that it totally suppresses α^2 isotropic Rayleigh scattering, helping to maximise the magnitude of the circular intensity differential Δ by ensuring that only anisotropic β^2 Rayleigh scattering contributes to the denominator. As an added benefit, β^2 scattering can be thought of as rotational ROA (incoherent to leading order) and that allows us to use the simpler single-molecule theory presented in chapter 1 as opposed to the far more complex liquid theory presented in chapter 2 despite working with a liquid sample. ICP with the scattered light analysed parallel to the scattering plane gives identical results to SCP with horizontally polarised incident light due to the principle of reciprocity [28, 50–52], as can be seen in table 1.1. Furthermore, we were not as interested in the $\alpha G'$ invariant as a way to obtain novel molecular information as that can already be measured via measurements of refraction and optical rotation. It is the β_A^2 and β_G^2 invariants that are unique to RayOA and those can be isolated from a right-angle SCP or ICP configuration. For these reasons, we opted for an SCP configuration with incident light polarised horizontally (parallel to the scattering plane).

In summary, we opted to focus on a laser wavelength $\lambda = 532\text{ nm}$, a scattering angle of $\xi = 90^\circ$ and an SCP configuration with horizontally polarised incident light. The RayOA circular intensity differential in this case has the form

$$\Delta = \frac{1}{c} \frac{24\beta_G^2 - 8\beta_A^2}{12\beta^2}, \quad (3.1)$$

which makes no reference to the isotropic Rayleigh scattering invariant α^2 or the isotropic RayOA invariant $\alpha G'$, these quantities being obtainable via independent measurements of refraction and optical rotation.

3.3 Choice of molecule

Next, we had to choose a small chiral molecule suitable as a target for first RayOA measurements. We wanted a molecule that could be purchased at low cost and high purity in both enantiomeric forms whilst being relatively safe to work with. Importantly,

the circular intensity differential Δ had to be large enough to be measured using our dedicated RayOA instrument, which was designed to operate to a precision of 10^{-5} as described in chapter 4.

3.4 Initial search and basic estimates

We began our search by identifying a wide range of small chiral molecules available from various chemical vendors. We then filtered these according to cost, availability of enantiomers, purity and other factors. For each of the candidate molecules that remained, we ran some basic quantum chemistry calculations with the Gaussian 09 [122] software at a low level of theory (uHF/6-311++G(d,p), an unrestricted Hartree-Fock method combined with a basis set that represents how electrons are distributed in a molecule) to get an approximate estimate of the expected circular intensity differential Δ . Some of our results are listed in Table 3.1. Note that these Δ values are meant to give a rough guide only. In order to calculate Δ accurately, significant computational power and sophistication is needed. More complex functionals like B3PW91, CAM-B3LYP, M06-2X etc. are commonly used utilising correlation-consistent Dunning basis sets like aug-cc-pVTZ. For those advanced calculations, we relied on our quantum chemistry collaborators, Dr. Andrew Puente and Prof. Prasad Polavarapu who provided us with those results; we expand on them in the following section.

Molecule	Phase, Solubility	$ \Delta /10^{-4}$
fluoxetine hydrochloride	crystalline solid, water solubility of 14 mg/mL	23.1
α -longipinene	liquid	13.3
longifolene	oily liquid	12.1
norpatchoulene	liquid	10.3
seychellene	liquid	9.1
α -cedrene	oily liquid	6.6
D-chiro-inositol	crystalline solid, water solubility of 75 mg/mL	4.9
α -pinene	liquid	5.0

Table 3.1: Phase and solubility information and basic estimates of the circular intensity differential Δ for a variety of candidate molecules. Molecular geometries were first optimised at the B3LYP/6-311++G(d,p) level of theory and the tensor components were calculated with uHF-6-311++G(d,p).

We eventually decided to reject molecules in solid form as that would further complicate the process of preparing our samples by introducing new variables (accuracy of solution percentage, choice of solvent etc.) and it would also require much more complex calculations to calculate the expected circular intensity differential value in Gaussian since it would then require an additional solvation model to account for solute-solvent interactions, which can skew the calculation results.

Ultimately, we decided to proceed with α -pinene. Although its predicted circular intensity differential values were not the largest among the candidates explored, it satisfied all the necessary requirements. α -pinene is a neat liquid with both enantiomers readily available in high purity analytical standards from commercial vendors such as Sigma. It is relatively inexpensive and with moderate volatility and safety concerns as to be easily handled in the laboratory. Additionally, it has been extensively studied in vibrational and electronic optical activity experiments which provided us with a useful reference in order to validate our findings. Finally, it is a rigid molecule without any significant conformers at room temperature, thereby eliminating conformational averaging effects that could otherwise complicate both experimental measurements and quantum chemistry calculations.

3.5 In-depth quantum-chemical calculations for α -pinene

Once we decided on α -pinene as our chosen molecule, we needed to perform some more in-depth quantum chemistry calculations in order to get the most accurate theoretical picture to compare with our experimental results. For this purpose, we relied on our collaborators Dr. Andrew R. Puente and Prof. Prasad L. Polavarapu (at the time, both at Vanderbilt University) who are computational chemists and had the required expertise and access to computational cluster facilities that allowed them to run all the calculations we needed for a comprehensive analysis of α -pinene.

Initially, a conformational analysis was performed on α -pinene by our collaborators using the Conflex software to determine how many stable conformers exist. Due to α -pinene having a very rigid structure, only one stable conformer of it exists which sim-

plifies further analysis greatly as no Boltzmann averaging is required between multiple conformers.

The geometry of the molecular structure was then optimised at the B3LYP/6-311++G(d,p) level as per Autschbach’s OR45 benchmark paper [123] using Gaussian 16. Frequency-specific polarisability tensor components were then calculated with the same software for our desired wavelength of 532 nm to construct the $\alpha_{\alpha\beta}$, $G'_{\alpha\beta}$ and $A_{\alpha,\beta\gamma}$ polarisability tensors relevant to RayOA. These were calculated at the DFT/aug-cc-pVTZ level with six different DFT density functionals. Amongst them there were two hybrid and most widely used functionals (B3LYP, B3PW91), three range-separated hybrid functionals that provide higher quality chiroptical results but are more intensive to run (CAM-B3LYP, ω HPBE and ω B97X-D) and a high-exchange functional from the Minnesota functional family (M06-2X). All six of them were used with the aug-cc-pVTZ augmented, correlation-consistent basis set which adds multiple diffuse functions (at a computational cost) but provides highly reliable results, especially for the $G'_{\alpha\beta}$ tensor which is notoriously sensitive to the choice of basis set. All these functionals are very commonly used in computational chemistry, especially with regards to chiroptical properties.

From these polarisability tensor results, the Rayleigh scattering invariants α^2 and β^2 and the RayOA invariants $\alpha G'$, β_G^2 and β_A^2 were constructed and the corresponding circular intensity differential Δ for each functional was calculated using (3.1). These results are presented in Table 3.2 for (1*R*,5*R*)- α -pinene. The predicted values of Δ are all clustered very closely together with a range that spans from -3.56×10^{-4} to -3.84×10^{-4} with an average value of -3.72×10^{-4} . This robustness of the computationally predicted Δ results across all these functionals demonstrates that a single-wavelength measurement of RayOA should be enough to correctly assign the absolute configuration of α -pinene (and most other small chiral molecules) according to the Zuber et al. hypothesis [14].

Functional	$\Delta/10^{-4}$	α^2	β^2	$\alpha G'$	β_G^2	β_A^2
B3LYP	-3.6813	14 353.88	300.5084	-1.6524	-7.9035	-0.9709
B3PW91	-3.5639	14 110.75	299.1693	-1.9694	-7.6203	-0.9447
CAM-B3LYP	-3.8390	13 713.50	269.5440	-2.1314	-7.4199	-0.9893
LC- ω HPBE	-3.7590	12 879.60	245.8982	-2.3956	-6.6538	-0.9615
M06-2X	-3.6558	13 720.30	275.2183	-2.1532	-7.1820	-0.8643
ω B97X-D	-3.8227	13 720.61	267.8240	-2.3126	-7.3401	-0.9757

Table 3.2: RayOA circular intensity differentials and invariants for (1*R*,5*R*)- α -pinene at $\lambda = 532$ nm, computed with six density functionals (Gaussian 16) at the aug-cc-pVTZ basis set in the gas phase. For all these calculations, the α -pinene geometry was optimised at the B3LYP/6-311++G(d,p) level. Listed quantities are the circular intensity differential Δ , the Rayleigh scattering invariants α^2 and β^2 and the RayOA invariants $\alpha G'$, β_G^2 and β_A^2 . Note that Δ is dimensionless and the invariants come by default in Hartree atomic units from Gaussian 16.

Chapter 4

Design of Dedicated RayOA Instrument

4.1 Introduction

In this chapter, we describe a new instrument designed to measure RayOA for small chiral molecules at a wavelength of $\lambda = 532\text{ nm}$ in a right-angled scattering geometry using an SCP configuration with horizontally polarised incident light. The quantity of central interest is the circular intensity differential

$$\Delta = \frac{1}{c} \frac{24\beta_G^2 - 8\beta_A^2}{12\beta^2}, \quad (4.1)$$

as seen in (3.1). Our instrument is designed to measure this Δ to a precision of 10^{-5} . The material in this chapter might serve as the basis of a patent application.

The equations in this chapter are mathematically complex but lead to relatively simple final results. The aim is to show that our instrument is capable of determining Δ accurately and to the desired precision *in spite of* the real-world imperfections embodied in our model by a plethora of mathematical parameters.

4.2 Overview

Below we give an overview of our instrument, illustrated in Fig. 4.1.

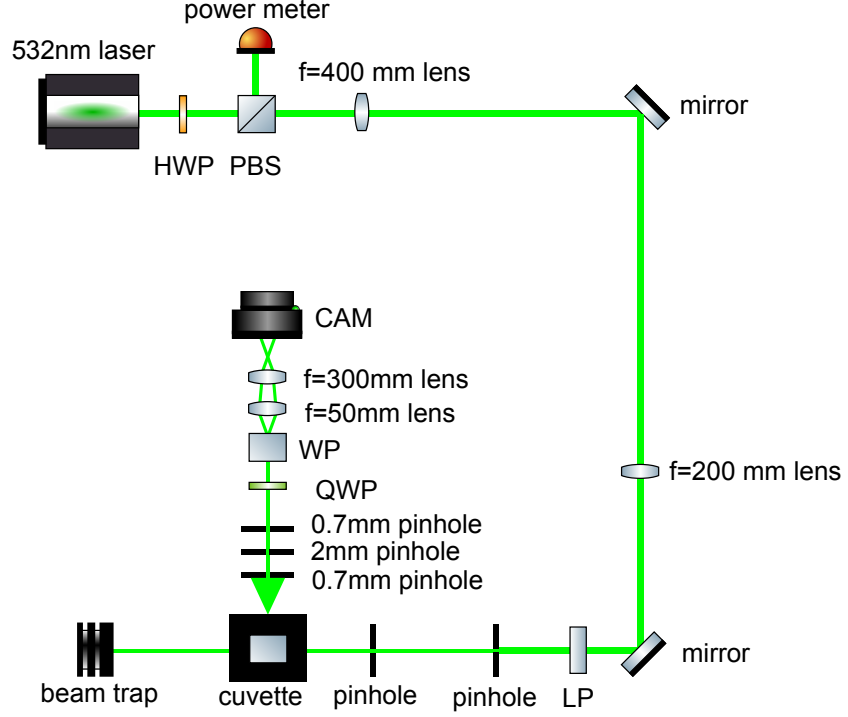


Figure 4.1: Overview of our instrument. Abbreviations are HWP: half-wave plate, PBS: polarising beam-splitter, LP: linear polariser, QWP: quarter-wave plate, WP: Wollaston prism, CAM: sCMOS camera sensor

Our light source is a diode pumped, solid state, continuous wave, green laser (CrystaLaser CL532-075-LO), emitting horizontally polarised light of central wavelength $\lambda = 532 \text{ nm}$ in a TEM_{00} mode with $M^2 < 1.1$ and a $1/e^2$ beam diameter of 0.36 mm at a power of $\sim 75 \text{ mW}$. It is ultra-low noise, with $< 1\%$ power stability (rms) over a 24-hour period. The laser is mounted on a temperature-controlled breadboard (Thorlabs PTC1/M) that uses thermoelectric elements and active air cooling to maintain a stable temperature of 25°C for optimal laser operation and stability. Pressure-activated, thermally conductive, double-sided tape (Thorlabs TCDT1) is employed between the laser unit and the breadboard to facilitate heat dissipation.

To control the power of laser light entering the instrument, the beam propagates

first through a rotatable AR-coated zero-order half-wave plate (Thorlabs WPH10M-532) followed by an AR-coated broadband polarising beam splitter cube (Thorlabs PBS 201), which reflects the vertically polarised component and transmits the horizontally polarised component with an extinction ratio of $> 10^3 : 1$. The half-wave plate and beamsplitter are tilted slightly to prevent the (faint) retroreflected beams from returning into the laser. Shown in Fig. 4.2 are plots of the laser power recorded using a USB power meter (Thorlabs PM16-121) at the beam splitter's reflected and transmitted ports as a function of the orientation of the half-wave plate. During a RayOA measurement, the power meter is located at the reflected port to gauge the power of the incident light ($l(t)$ below) in real time.

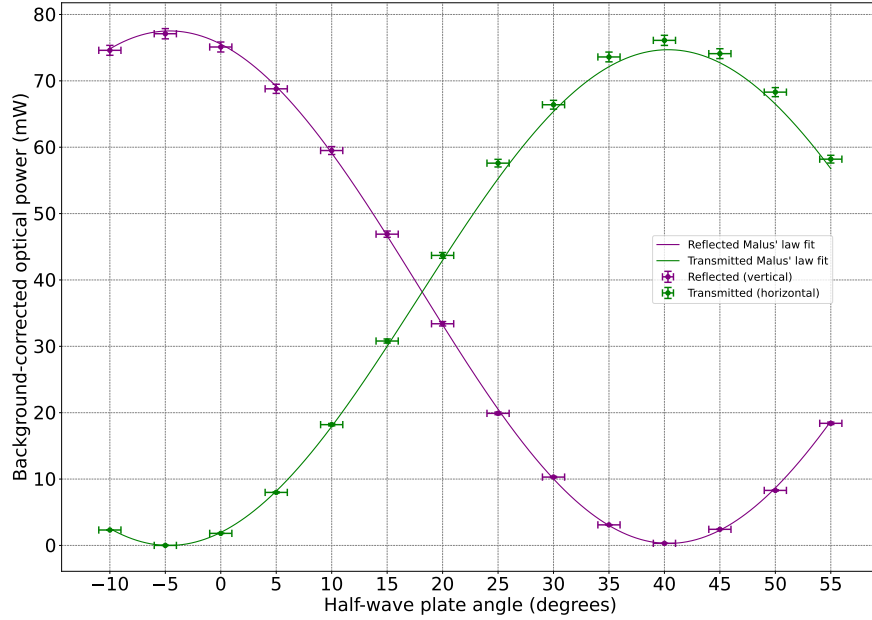


Figure 4.2: Laser power at the transmission and reflection ports of the beam splitter as a function of the half-wave plate angle. The 5° angular offset is due to the mismatch of the HWP axis with the angle markings on the rotation mount and the slight deviation from Malus' law in the transmitted power curve might be due to the beam wandering off the power meter.

Next, the beam propagates through an AR-coated plano-convex lens with a focal length of 400 mm (Thorlabs LA1172-A-ML) before being reflected at right angles by an aluminium mirror (Thorlabs ME1-G01) with a reflectivity of $89.1 \pm 0.3\%$ measured in situ. The beam then propagates through an AR-coated plano-convex lens with a focal length of 200 mm (Thorlabs LA1708-A-ML) before being reflected through right angles

again by a mirror (Thorlabs ME1-G01) with a reflectivity of $84.3 \pm 0.3\%$ measured in situ. The lenses are separated by a geometrical path length of ~ 50 cm, shrinking the beam by a factor of ~ 2 to prevent diffraction as it propagates through the pinholes following the LP. The mirrors give control over the height and angle of the beam directed towards the sample.

The beam then propagates through a horizontal linear polariser (Thorlabs LPVISC100-MP2) with an extinction ratio of $> 10^5 : 1$ and a transmission of $67 \pm 1\%$ measured in situ. The polariser fixes the polarisation azimuth of the incident light to be $\theta^i = 90.00 \pm 0.25$. Together with the beam splitter, it should also ensure that the ellipticity of the incident light is $\eta^i < 1/\sqrt{1 \times 10^{3+5}} = 1 \times 10^{-4}$ rad. We note here, however, that this ignores possible polarisation changes upon reflection by the mirrors; an oversight to be corrected in future iterations of our instrument.

A liquid or solution sample is held in a $10 \text{ mm} \times 10 \text{ mm}$ high precision quartz glass macro cell (Hellma HL117100F-10-40), which is held in turn by a cuvette holder (Thorlabs CVH100/M) with all four ports (entrance, transmission, scattering, spare) open. At least 2 cm^3 of liquid is used and care is taken to ensure that the beam propagates equidistant from the bottom of the cell and the liquid surface.

At the transmission port a beam trap (Thorlabs BT600/M) terminates the laser beam with a total integrated backscatter fraction $< 9 \times 10^{-5}$ at 633 nm .

At the scattering port we have two $700 \mu\text{m} \pm 10 \mu\text{m}$ pinholes (Thorlabs P700K) sandwiching a $2.00 \text{ mm} \pm 10 \mu\text{m}$ pinhole (Thorlabs P2000K) with a spacing of 5 cm between each. These allow a tiny solid angle of $(1.83 \pm 0.14) \times 10^{-5} \text{ sr}$ of Rayleigh scattered light to pass, where we have taken the final pinhole to be located $14.5 \pm 0.5 \text{ cm}$ from the centre of the cuvette. The central pinhole also helps in minimising light that has reflected multiple times within this section of the detection train to transmit through the final pinhole.

The degree of circularity of the Rayleigh scattered light is probed by the high-precision detection system described and theoretically modelled in detail in the next section.

The incident light propagates through two $3.00\text{ mm} \pm 40\text{ }\mu\text{m}$ pinholes (Thorlabs P3000K) separated by 5 cm before entering the cuvette holder. Except for these, there is no scope for external light to enter the detection train, as extensive shielding, not shown in Fig. 4.1, is realised using light-tight tubes (Thorlabs SM1L20), black masking tape (Thorlabs T137-1.0) and further housings made of black cardboard. To minimise the effects of stray light within this environment, internal faces are coated where possible in Musou black water-based acrylic paint, which boasts 98.8% visible light absorption when applied using a paint brush [124].

4.3 High-precision detection system

In this section, we present a detailed description and theoretical model of the high-precision detection system. Our aim is to show that this system can accurately determine the RayOA circular intensity differentials $\Delta(S) = -\Delta(R)$ for opposite molecular enantiomers down to the 10^{-5} level in spite of the many imperfections inherent to its components. The model is based on the Jones and Mueller formalisms summarised in Sec. 1.3.4. A simplified schematic of the detection system is depicted in Fig. 4.3.

Let us suppose that the Mueller vector of the scattered light entering the detection system has the form

$$\ell(t)S(t) = \ell(t) \begin{pmatrix} S_0(t) \\ S_1(t) \\ S_2(t) \\ S_3(t) \end{pmatrix}, \quad (4.2)$$

where $\ell(t)$ is a modulating factor accounting for possible time variations of the incident laser power and $S_0(t)$, $S_1(t)$, $S_2(t)$ and $S_3(t)$ are the Stokes parameters of the scattered light, in general time dependent due to fluctuations in the sample. We do not account explicitly for spatial variation of the Stokes parameters in our model as the solid angle of scattered light entering the detection system is tiny.

The scattered light is incident first upon an AR-coated zero-order quarter-wave

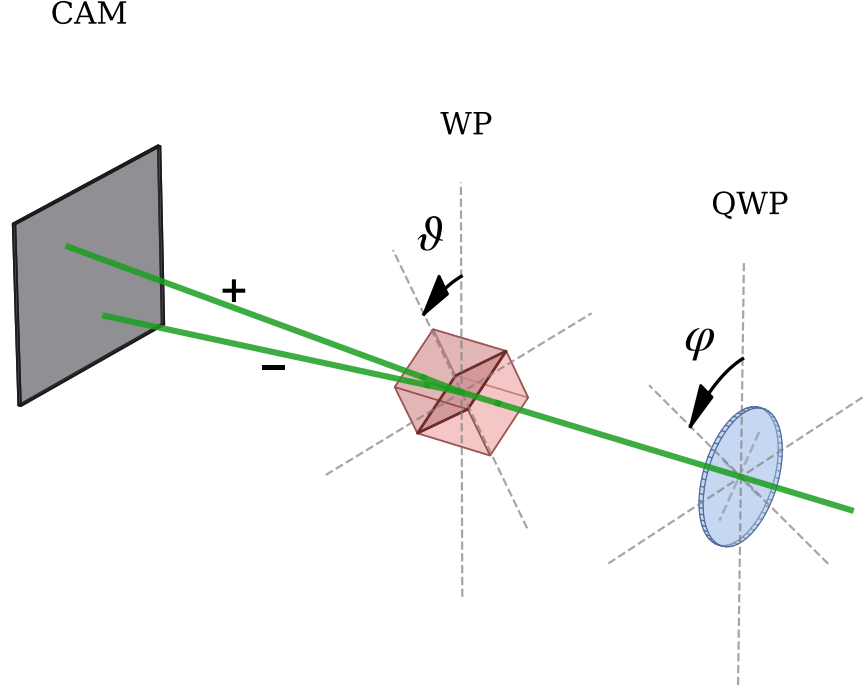


Figure 4.3: Simplified overview of our detection train setup. A rotatable quarter-wave plate (QWP) followed by an independently rotatable Wollaston prism (WP) that “splits” the beam into two mutually orthogonal polarised beams and finally a camera (CAM) for detection. Note that the two lenses in between the WP and the CAM used to focus the diverging beams onto the sensor have been omitted in this figure for the sake of simplicity along with all the light shielding that was used in the actual setup.

plate (“QWP”; Thorlabs WPQ10M-532) with a retardance error of $< \lambda/300$, held in a motorised rotation mount (“Imho”¹; Thorlabs K10CR1/M). The QWP ideally converts orthogonal circular polarisations into orthogonal linear polarisations. We take the Jones matrix of the QWP to have the form

$$\tilde{J}_{\text{QWP}}(\varphi) \propto R(\varphi) \begin{pmatrix} 1 & \tilde{\alpha} \\ \tilde{\beta} & ie^{i\tilde{\gamma}} \end{pmatrix} R^T(\varphi), \quad (4.3)$$

where φ is an angle describing the orientation of the QWP; $\tilde{\alpha} = \alpha + i\alpha'$, $\tilde{\beta} = \beta + i\beta'$ and $\tilde{\gamma} = \gamma + i\gamma'$ account for possible imperfections and R is a rotation matrix of the form shown in equation (1.44). Note that φ is related to the angle φ_{Imho} quoted by Imhotep

¹“Imho” is short for “Imhotep”; the villain from 1999 action/adventure film The Mummy.

via

$$\varphi = \varphi_{\text{Imho}} - \varphi_0, \quad (4.4)$$

where φ_0 is an angular offset.

After propagating through the QWP, the scattered light is incident upon an AR-coated Wollaston prism (“WP”; Thorlabs WP10-A) with an extinction ratio of $> 10^5 : 1$, also held in a motorised rotation mount (“Anck”²; Thorlabs K10CR1/M). The WP ideally refracts orthogonal linear polarisation states into two diverging outputs with an angular separation of about 20° . We take the Jones matrices of the WP to have the form

$$\tilde{J}_{+, \text{WP}}(\vartheta) \propto R(\vartheta) \begin{pmatrix} 1 & \tilde{\delta}_+ \\ \tilde{\epsilon}_+ & \tilde{\zeta}_+ \end{pmatrix} R^T(\vartheta) \quad (4.5)$$

$$\tilde{J}_{-, \text{WP}}(\vartheta) \propto R(\vartheta) \begin{pmatrix} \tilde{\zeta}_- & \tilde{\epsilon}_- \\ \tilde{\delta}_- & 1 \end{pmatrix} R^T(\vartheta), \quad (4.6)$$

where ϑ is an angle that describes the orientation of the WP; $\tilde{\delta}_\pm$, $\tilde{\epsilon}_\pm$ and $\tilde{\zeta}_\pm$ account for possible imperfections and the $\pm$ signs distinguish between the outputs. Note that ϑ is related to the angle ϑ_{Anck} quoted by Anck via

$$\vartheta = \vartheta_{\text{Anck}} - \vartheta_0, \quad (4.7)$$

where ϑ_0 is an angular offset.

The Jones matrices describing the QWP and WP together are

$$\tilde{J}_\pm(\vartheta, \varphi) \propto \tilde{J}_{\pm, \text{WP}}(\vartheta) \tilde{J}_{\text{QWP}}(\varphi). \quad (4.8)$$

Explicit substitution of (4.3), (4.5) and (4.6) into (4.8) making use of (1.44) reveals that

²“Anck” is short for “Anck-su-namun”; Imhotep’s forbidden lover.

the matrix elements of $\tilde{J}_\pm(\vartheta, \varphi)$ are

$$\begin{aligned}
 [\tilde{J}_+(\vartheta, \varphi)]_{xx} \propto & \cos \vartheta \cos \chi \cos \varphi + ie^{i\tilde{\gamma}} \cos \vartheta \sin \chi \sin \varphi + \tilde{\alpha} \cos \vartheta \cos \chi \sin \varphi \\
 & + \tilde{\beta} \cos \vartheta \sin \chi \cos \varphi - \tilde{\delta}_+ \cos \vartheta \sin \chi \cos \varphi + \tilde{\epsilon}_+ \sin \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\zeta}_+ \sin \vartheta \sin \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_+ \cos \vartheta \cos \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_+ \sin \vartheta \sin \chi \sin \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_+ \sin \vartheta \cos \chi \sin \varphi - \tilde{\alpha} \tilde{\delta}_+ \cos \vartheta \sin \chi \sin \varphi + \tilde{\alpha} \tilde{\epsilon}_+ \sin \vartheta \cos \chi \sin \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_+ \sin \vartheta \sin \chi \sin \varphi + \tilde{\beta} \tilde{\delta}_+ \cos \vartheta \cos \chi \cos \varphi + \tilde{\beta} \tilde{\epsilon}_+ \sin \vartheta \sin \chi \cos \varphi \\
 & + \tilde{\beta} \tilde{\zeta}_+ \sin \vartheta \cos \chi \cos \varphi, \tag{4.9}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_+(\vartheta, \varphi)]_{xy} \propto & -\cos \vartheta \cos \chi \sin \varphi + ie^{i\tilde{\gamma}} \cos \vartheta \sin \chi \cos \varphi + \tilde{\alpha} \cos \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\beta} \cos \vartheta \sin \chi \sin \varphi + \tilde{\delta}_+ \cos \vartheta \sin \chi \sin \varphi - \tilde{\epsilon}_+ \sin \vartheta \cos \chi \sin \varphi \\
 & + \tilde{\zeta}_+ \sin \vartheta \sin \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_+ \cos \vartheta \cos \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_+ \sin \vartheta \sin \chi \cos \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_+ \sin \vartheta \cos \chi \cos \varphi - \tilde{\alpha} \tilde{\delta}_+ \cos \vartheta \sin \chi \cos \varphi + \tilde{\alpha} \tilde{\epsilon}_+ \sin \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_+ \sin \vartheta \sin \chi \cos \varphi - \tilde{\beta} \tilde{\delta}_+ \cos \vartheta \cos \chi \sin \varphi - \tilde{\beta} \tilde{\epsilon}_+ \sin \vartheta \sin \chi \sin \varphi \\
 & - \tilde{\beta} \tilde{\zeta}_+ \sin \vartheta \cos \chi \sin \varphi, \tag{4.10}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_+(\vartheta, \varphi)]_{yx} \propto & -\sin \vartheta \cos \chi \cos \varphi - ie^{i\tilde{\gamma}} \sin \vartheta \sin \chi \sin \varphi - \tilde{\alpha} \sin \vartheta \cos \chi \sin \varphi \\
 & - \tilde{\beta} \sin \vartheta \sin \chi \cos \varphi + \tilde{\delta}_+ \sin \vartheta \sin \chi \cos \varphi + \tilde{\epsilon}_+ \cos \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\zeta}_+ \cos \vartheta \sin \chi \cos \varphi - ie^{i\tilde{\gamma}} \tilde{\delta}_+ \sin \vartheta \cos \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_+ \cos \vartheta \sin \chi \sin \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_+ \cos \vartheta \cos \chi \sin \varphi + \tilde{\alpha} \tilde{\delta}_+ \sin \vartheta \sin \chi \sin \varphi + \tilde{\alpha} \tilde{\epsilon}_+ \cos \vartheta \cos \chi \sin \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_+ \cos \vartheta \sin \chi \sin \varphi - \tilde{\beta} \tilde{\delta}_+ \sin \vartheta \cos \chi \cos \varphi + \tilde{\beta} \tilde{\epsilon}_+ \cos \vartheta \sin \chi \cos \varphi \\
 & + \tilde{\beta} \tilde{\zeta}_+ \cos \vartheta \cos \chi \cos \varphi \tag{4.11}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_+(\vartheta, \varphi)]_{yy} \propto & \sin \vartheta \cos \chi \sin \varphi - ie^{i\tilde{\gamma}} \sin \vartheta \sin \chi \cos \varphi - \tilde{\alpha} \sin \vartheta \cos \chi \cos \varphi \\
 & + \tilde{\beta} \sin \vartheta \sin \chi \sin \varphi - \tilde{\delta}_+ \sin \vartheta \sin \chi \sin \varphi - \tilde{\epsilon}_+ \cos \vartheta \cos \chi \sin \varphi \\
 & + \tilde{\zeta}_+ \cos \vartheta \sin \chi \sin \varphi - ie^{i\tilde{\gamma}} \tilde{\delta}_+ \sin \vartheta \cos \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_+ \cos \vartheta \sin \chi \cos \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_+ \cos \vartheta \cos \chi \cos \varphi + \tilde{\alpha} \tilde{\delta}_+ \sin \vartheta \sin \chi \cos \varphi + \tilde{\alpha} \tilde{\epsilon}_+ \cos \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_+ \cos \vartheta \sin \chi \cos \varphi + \tilde{\beta} \tilde{\delta}_+ \sin \vartheta \cos \chi \sin \varphi - \tilde{\beta} \tilde{\epsilon}_+ \cos \vartheta \sin \chi \sin \varphi \\
 & - \tilde{\beta} \tilde{\zeta}_+ \cos \vartheta \cos \chi \sin \varphi \tag{4.12}
 \end{aligned}$$

for the + output and

$$\begin{aligned}
 [\tilde{J}_-(\vartheta, \varphi)]_{xx} \propto & -\sin \vartheta \sin \chi \cos \varphi + ie^{i\tilde{\gamma}} \sin \vartheta \cos \chi \sin \varphi - \tilde{\alpha} \sin \vartheta \sin \chi \sin \varphi \\
 & + \tilde{\beta} \sin \vartheta \cos \chi \cos \varphi + \tilde{\delta}_- \sin \vartheta \cos \chi \cos \varphi - \tilde{\epsilon}_- \cos \vartheta \sin \chi \cos \varphi \\
 & + \tilde{\zeta}_- \cos \vartheta \cos \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_- \sin \vartheta \sin \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_- \cos \vartheta \cos \chi \sin \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_- \cos \vartheta \sin \chi \sin \varphi + \tilde{\alpha} \tilde{\delta}_- \sin \vartheta \cos \chi \sin \varphi - \tilde{\alpha} \tilde{\epsilon}_- \cos \vartheta \sin \chi \sin \varphi \\
 & + \tilde{\alpha} \tilde{\zeta}_- \cos \vartheta \cos \chi \sin \varphi + \tilde{\beta} \tilde{\delta}_- \sin \vartheta \sin \chi \cos \varphi + \tilde{\beta} \tilde{\epsilon}_- \cos \vartheta \cos \chi \cos \varphi \\
 & + \tilde{\beta} \tilde{\zeta}_- \cos \vartheta \sin \chi \cos \varphi, \tag{4.13}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_-(\vartheta, \varphi)]_{xy} \propto & +\sin \vartheta \sin \chi \sin \varphi + ie^{i\tilde{\gamma}} \sin \vartheta \cos \chi \cos \varphi - \tilde{\alpha} \sin \vartheta \sin \chi \cos \varphi \\
 & - \tilde{\beta} \sin \vartheta \cos \chi \sin \varphi - \tilde{\delta}_- \sin \vartheta \cos \chi \sin \varphi + \tilde{\epsilon}_- \cos \vartheta \sin \chi \sin \varphi \\
 & - \tilde{\zeta}_- \cos \vartheta \cos \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_- \sin \vartheta \sin \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\epsilon}_- \cos \vartheta \cos \chi \cos \varphi \\
 & + ie^{i\tilde{\gamma}} \tilde{\zeta}_- \cos \vartheta \sin \chi \cos \varphi + \tilde{\alpha} \tilde{\delta}_- \sin \vartheta \cos \chi \cos \varphi - \tilde{\alpha} \tilde{\epsilon}_- \cos \vartheta \sin \chi \cos \varphi \\
 & + \tilde{\alpha} \tilde{\zeta}_- \cos \vartheta \cos \chi \cos \varphi - \tilde{\beta} \tilde{\delta}_- \sin \vartheta \sin \chi \sin \varphi - \tilde{\beta} \tilde{\epsilon}_- \cos \vartheta \cos \chi \sin \varphi \\
 & - \tilde{\beta} \tilde{\zeta}_- \cos \vartheta \sin \chi \sin \varphi, \tag{4.14}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_-(\vartheta, \varphi)]_{yx} \propto & -\cos \vartheta \sin \chi \cos \varphi + ie^{i\tilde{\gamma}} \cos \vartheta \cos \chi \sin \varphi - \tilde{\alpha} \cos \vartheta \sin \chi \sin \varphi \\
 & + \tilde{\beta} \cos \vartheta \cos \chi \cos \varphi + \tilde{\delta}_- \cos \vartheta \cos \chi \cos \varphi + \tilde{\epsilon}_- \sin \vartheta \sin \chi \cos \varphi \\
 & - \tilde{\zeta}_- \sin \vartheta \cos \chi \cos \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_- \cos \vartheta \sin \chi \sin \varphi - ie^{i\tilde{\gamma}} \tilde{\epsilon}_- \sin \vartheta \cos \chi \sin \varphi \\
 & - ie^{i\tilde{\gamma}} \tilde{\zeta}_- \sin \vartheta \sin \chi \sin \varphi + \tilde{\alpha} \tilde{\delta}_- \cos \vartheta \cos \chi \sin \varphi + \tilde{\alpha} \tilde{\epsilon}_- \sin \vartheta \sin \chi \sin \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_- \sin \vartheta \cos \chi \sin \varphi + \tilde{\beta} \tilde{\delta}_- \cos \vartheta \sin \chi \cos \varphi - \tilde{\beta} \tilde{\epsilon}_- \sin \vartheta \cos \chi \cos \varphi \\
 & - \tilde{\beta} \tilde{\zeta}_- \sin \vartheta \sin \chi \cos \varphi \tag{4.15}
 \end{aligned}$$

$$\begin{aligned}
 [\tilde{J}_-(\vartheta, \varphi)]_{yy} \propto & +\cos \vartheta \sin \chi \sin \varphi + ie^{i\tilde{\gamma}} \cos \vartheta \cos \chi \cos \varphi - \tilde{\alpha} \cos \vartheta \sin \chi \cos \varphi \\
 & - \tilde{\beta} \cos \vartheta \cos \chi \sin \varphi - \tilde{\delta}_- \cos \vartheta \cos \chi \sin \varphi - \tilde{\epsilon}_- \sin \vartheta \sin \chi \sin \varphi \\
 & + \tilde{\zeta}_- \sin \vartheta \cos \chi \sin \varphi + ie^{i\tilde{\gamma}} \tilde{\delta}_- \cos \vartheta \sin \chi \cos \varphi - ie^{i\tilde{\gamma}} \tilde{\epsilon}_- \sin \vartheta \cos \chi \cos \varphi \\
 & - ie^{i\tilde{\gamma}} \tilde{\zeta}_- \sin \vartheta \sin \chi \cos \varphi + \tilde{\alpha} \tilde{\delta}_- \cos \vartheta \cos \chi \cos \varphi + \tilde{\alpha} \tilde{\epsilon}_- \sin \vartheta \sin \chi \cos \varphi \\
 & - \tilde{\alpha} \tilde{\zeta}_- \sin \vartheta \cos \chi \cos \varphi - \tilde{\beta} \tilde{\delta}_- \cos \vartheta \sin \chi \sin \varphi + \tilde{\beta} \tilde{\epsilon}_- \sin \vartheta \cos \chi \sin \varphi \\
 & + \tilde{\beta} \tilde{\zeta}_- \sin \vartheta \sin \chi \sin \varphi \tag{4.16}
 \end{aligned}$$

for the $-$ output, where

$$\chi = \varphi - \vartheta \quad (4.17)$$

is an angle describing the orientation of the QWP relative to the WP. Using (4.9)-(4.17) in (1.24)-(1.39) reveals that the Mueller matrices $[M_{\pm}(\vartheta, \varphi)]$ describing the QWP and WP together have matrix elements

$$\begin{aligned} [M_{\pm}(\vartheta, \varphi)]_{00} = & \frac{1}{2}[1 - \gamma'(\delta_+ + \delta_-) \sin(2\chi) + (\alpha' + \beta)(\delta_+ + \delta_-) \cos(2\chi)] \\ & \pm \frac{1}{2} \left\{ -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) \right. \\ & + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) \\ & + [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_-)\gamma'] \sin(2\chi) \\ & \left. + \left[\gamma' + \frac{1}{2}(|\tilde{\alpha}|^2 - |\tilde{\beta}|^2) + (\alpha' + \beta)(\delta_+ - \delta_-) \right] \cos(2\chi) \right\} + \dots, \quad (4.18) \end{aligned}$$

$$\begin{aligned} [M_{\pm}(\vartheta, \varphi)]_{01} = & \frac{1}{2}[(\alpha + \beta') \sin(2\varphi) + \gamma' \cos(2\varphi) - (\delta'_+ - \delta'_-) \sin(2\varphi) \\ & - (\delta_+ + \delta_-) \cos(2\varphi) \sin(2\chi)] \\ & \pm \frac{1}{2} \left\{ \cos(2\varphi) \cos(2\chi) - (\delta'_+ + \delta'_-) \sin(2\varphi) \right. \\ & - [\gamma \sin(2\varphi) + (\alpha' - \beta + \delta_+ - \delta_-) \cos(2\varphi)] \sin(2\chi) \\ & \left. + (\alpha - \beta') \sin(2\varphi) \cos(2\chi) \right\} + \dots, \quad (4.19) \end{aligned}$$

$$\begin{aligned} [M_{\pm}(\vartheta, \varphi)]_{02} = & \frac{1}{2}[-(\alpha + \beta') \cos(2\varphi) + \gamma' \sin(2\varphi) + (\delta'_+ - \delta'_-) \cos(2\varphi) \\ & - (\delta_+ + \delta_-) \sin(2\varphi) \sin(2\chi)] \\ & \pm \frac{1}{2} \left\{ \sin(2\varphi) \cos(2\chi) + (\delta'_+ + \delta'_-) \cos(2\varphi) \right. \\ & + [\gamma \cos(2\varphi) - (\alpha' - \beta + \delta_+ - \delta_-) \sin(2\varphi)] \sin(2\chi) \\ & \left. - (\alpha - \beta') \cos(2\varphi) \cos(2\chi) \right\} + \dots \quad (4.20) \end{aligned}$$

$$[M_{\pm}(\vartheta, \varphi)]_{03} = \pm \frac{1}{2} \sin(2\chi) + \dots, \quad (4.21)$$

where we have normalised $[M_{\pm}(\vartheta, \varphi)]$ such that

$$\frac{1}{4\pi^2} \int_0^{2\pi} \int_0^{2\pi} [M_+(\vartheta, \varphi) + M_-(\vartheta, \varphi)] S(t) d\varphi d\vartheta = S_0(t) \quad (4.22)$$

and explicitly quoted $[M_{\pm}(\vartheta, \varphi)]_{00}$ to second order in the imperfection parameters $\tilde{\alpha}$, $\tilde{\beta}$, $\tilde{\gamma}$, $\tilde{\delta}_{\pm}$, $\tilde{\epsilon}_{\pm}$ and $\tilde{\zeta}_{\pm}$; $[M_{\pm}(\vartheta, \varphi)]_{01}$ and $[M_{\pm}(\vartheta, \varphi)]_{02}$ to first order and $[M_{\pm}(\vartheta, \varphi)]_{03}$ to zeroth order in anticipation of the hierarchy $S_0 > S_1 > S_2 > S_3$ described below. The reader might find it helpful to note that (4.18)-(4.21) reduces to

$$[M_{\pm}(\vartheta, \varphi)]_{00} = \frac{1}{2}, \quad (4.23)$$

$$[M_{\pm}(\vartheta, \varphi)]_{01} = \pm \frac{1}{2} \cos(2\varphi) \cos(2\chi), \quad (4.24)$$

$$[M_{\pm}(\vartheta, \varphi)]_{02} = \pm \frac{1}{2} \sin(2\varphi) \cos(2\chi) \quad (4.25)$$

$$[M_{\pm}(\vartheta, \varphi)]_{03} = \pm \frac{1}{2} \sin(2\chi) \quad (4.26)$$

for the idealised case where the QWP and WP have no imperfections ($\tilde{\alpha} = \tilde{\beta} = \tilde{\gamma} = \tilde{\delta}_{\pm} = \tilde{\epsilon}_{\pm} = \tilde{\zeta}_{\pm} = 0$).

Following the WP, a pair of AR-coated lenses (Thorlabs LA1131-A-ML and Thorlabs LA1484-A) separated by ~ 2 cm collimates and focusses the scattered light in the $\pm$ outputs.

The scattered light in the collimated and focussed $\pm$ outputs eventually intersects the sensor plane of a 5.5MP sCMOS camera (“CAM”; Andor ZL41 Wave sCMOS), ideally resulting in two spatially separated and polarisation dependent images of the incident laser beam as seen through the pinholes due to Rayleigh scattering. Taking a finite exposure of duration Δt from time t_n to time $t_n + \Delta t$, performing background subtraction and spatially integrating over the $\pm$ images yields the n th pair of measured

$\pm$ signals (measured in units of “average counts per pixel” or just “counts” for short) as

$$\begin{aligned}
 \langle I_{\pm} \rangle_n(\vartheta, \varphi) &= \langle b_{\pm} \rangle_n(\vartheta) \\
 &+ \frac{1}{2} \eta_{\pm}(\vartheta, \varphi) [C_0(\chi) \langle \ell S_0 \rangle_n + C_1(\chi) \langle \ell S'_1 \rangle_n(\varphi) \\
 &+ C_2(\chi) \langle \ell S'_2 \rangle_n(\varphi) + C_3(\chi) \langle \ell S_3 \rangle_n] \\
 &\pm \frac{1}{2} \eta_{\pm}(\vartheta, \varphi) [D_0(\chi) \langle \ell S_0 \rangle_n + D_1(\chi) \langle \ell S'_1 \rangle_n(\varphi) \\
 &+ D_2(\chi) \langle \ell S'_2 \rangle_n(\varphi) + D_3(\chi) \langle \ell S_3 \rangle_n]
 \end{aligned} \tag{4.27}$$

with

$$C_0(\chi) = 1 - \gamma'(\delta_+ + \delta_-) \sin(2\chi) + (\alpha' + \beta)(\delta_+ + \delta_-) \cos(2\chi), \tag{4.28}$$

$$C_1(\chi) = \gamma' - (\delta_+ + \delta_-) \sin(2\chi), \tag{4.29}$$

$$C_2(\chi) = -\alpha - \beta' + \delta'_+ - \delta'_-, \tag{4.30}$$

$$C_3(\chi) = 0, \tag{4.31}$$

$$\begin{aligned}
 D_0(\chi) &= -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\
 &+ \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) + [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_-)\gamma'] \sin(2\chi) \\
 &+ \left[\gamma' + \frac{1}{2}(|\tilde{\alpha}|^2 - |\tilde{\beta}|^2) + (\alpha' + \beta)(\delta_+ - \delta_-) \right] \cos(2\chi),
 \end{aligned} \tag{4.32}$$

$$D_1(\chi) = \cos(2\chi) - (\alpha' - \beta + \delta_+ - \delta_-) \sin(2\chi), \tag{4.33}$$

$$D_2(\chi) = \delta'_+ + \delta'_- + \gamma \sin(2\chi) - (\alpha - \beta') \cos(2\chi), \tag{4.34}$$

$$D_3(\chi) = \sin(2\chi), \tag{4.35}$$

$$S'_1(\varphi, t) = \cos(2\varphi) S_1(t) + \sin(2\varphi) S_2(t) \tag{4.36}$$

$$S'_2(\varphi, t) = -\sin(2\varphi) S_1(t) + \cos(2\varphi) S_2(t), \tag{4.37}$$

where $\langle b_{\pm} \rangle_n(\vartheta)$ are background fluctuation contributions; $\eta_{\pm}(\vartheta, \varphi)$ are effective detection efficiencies, accounting for overall losses in the QWP, WP, lenses and the CAM whilst converting units; $C_0(\chi)$, $C_1(\chi)$, $C_2(\chi)$, $C_3(\chi)$, $D_0(\chi)$, $D_1(\chi)$, $D_2(\chi)$ and $D_3(\chi)$ are shorthands; $S'_1(\varphi, t)$ and $S'_2(\varphi, t)$ are Stokes parameters of the scattered light defined

relative to the axes of the QWP rather than the laboratory and we use angular brackets to indicate the time averaging inherent to the exposure. The $\langle b_{\pm} \rangle_n(\vartheta)$ values depend on ϑ but not φ as the locations of the $\pm$ images vary significantly with the orientation of the WP but we assume the $\pm$ spatial integration regions to be chosen independent of the orientation of the QWP. We allow $\eta_{\pm}(\vartheta, \varphi)$ to vary with φ as well as ϑ to account for a slight but important movement of the $\pm$ images with changes in the orientation of the QWP. We do not account explicitly for the polarisation sensitivity of the CAM in our model, as this should be minimised by our choice of $\vartheta = -45^\circ + \delta\vartheta$ in the A and B configurations described below. The reader might find it helpful to note that (4.27) reduces to

$$\langle I_{\pm} \rangle_n(\vartheta, \varphi) \propto \frac{1}{2} \langle \ell S_0 \rangle_n \pm \frac{1}{2} [\cos(2\chi) \langle \ell S'_1 \rangle_n + \sin(2\chi) \langle \ell S_3 \rangle_n] \quad (4.38)$$

for the idealised case where the QWP and WP have no imperfections ($\tilde{\alpha} = \tilde{\beta} = \tilde{\gamma} = \tilde{\delta}_{\pm} = \tilde{\epsilon}_{\pm} = \tilde{\zeta}_{\pm} = 0$), the CAM has a constant background that has been perfectly subtracted ($\langle b_{\pm} \rangle_n(\vartheta) = 0$) and there is no effective detection efficiency imbalance ($\eta_+(\vartheta, \varphi) = \eta_-(\vartheta, \varphi)$).

The n th pair of measured $\pm$ signals $\langle I_{\pm} \rangle_n(\vartheta, \varphi)$ can be used to construct the n th dimensionless ratio

$$\Delta_n(\vartheta, \varphi) = \frac{\langle I_+ \rangle_n(\vartheta, \varphi) - \langle I_- \rangle_n(\vartheta, \varphi)}{\langle I_+ \rangle_n(\vartheta, \varphi) + \langle I_- \rangle_n(\vartheta, \varphi)}. \quad (4.39)$$

Explicit substitution of (4.27) into (4.39) gives

$$\Delta_n(\vartheta, \varphi) = \Delta_{n,\text{background}}(\vartheta, \varphi) + \Delta_{n,\text{imbalance}}(\vartheta, \varphi) + \Delta_{n,\text{polarisation}}(\vartheta, \varphi) \quad (4.40)$$

with

$$\begin{aligned}\Delta_{n,\text{background}}(\vartheta, \varphi) &= \frac{2\langle\delta b\rangle_n(\vartheta)}{\bar{\eta}(\vartheta, \varphi)\langle\ell S_0\rangle_n}U(\vartheta, \varphi), \\ \Delta_{n,\text{imbalance}}(\vartheta, \varphi) &= \frac{\delta\eta(\vartheta, \varphi)}{\bar{\eta}(\vartheta, \varphi)} \left[C_0(\chi) + C_1(\chi) \frac{\langle\ell S'_1\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} \right. \\ &\quad \left. + C_2(\chi) \frac{\langle\ell S'_2\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + C_3(\chi) \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \right] U(\vartheta, \varphi)\end{aligned}\quad (4.41)$$

$$\begin{aligned}\Delta_{n,\text{polarisation}}(\vartheta, \varphi) &= \left[D_0(\chi) + D_1(\chi) \frac{\langle\ell S'_1\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} \right. \\ &\quad \left. + D_2(\chi) \frac{\langle\ell S'_2\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + D_3(\chi) \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \right] U(\vartheta, \varphi)\end{aligned}\quad (4.42)$$

using

$$\begin{aligned}U(\vartheta, \varphi) &= \left\{ C_0(\chi) + C_1(\chi) \frac{\langle\ell S'_1\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + C_2(\chi) \frac{\langle\ell S'_2\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + C_3(\chi) \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \right. \\ &\quad \left. + \frac{\delta\eta(\vartheta, \varphi)}{\bar{\eta}(\vartheta, \varphi)} \left[D_0(\chi) + D_1(\chi) \frac{\langle\ell S'_1\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + D_2(\chi) \frac{\langle\ell S'_2\rangle_n(\varphi)}{\langle\ell S_0\rangle_n} + D_3(\chi) \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \right] \right. \\ &\quad \left. + \frac{2\langle\bar{b}\rangle_n(\vartheta)}{\bar{\eta}(\vartheta, \varphi)\langle\ell S_0\rangle_n} \right\}^{-1}\end{aligned}\quad (4.43)$$

together with

$$\langle\bar{b}\rangle_n(\vartheta) = \frac{1}{2}[\langle b_+\rangle_n(\vartheta) + \langle b_-\rangle_n(\vartheta)], \quad (4.44)$$

$$\langle\delta b\rangle_n(\vartheta) = \frac{1}{2}[\langle b_+\rangle_n(\vartheta) - \langle b_-\rangle_n(\vartheta)], \quad (4.45)$$

$$\bar{\eta}(\vartheta, \varphi) = \frac{1}{2}[\eta_+(\vartheta, \varphi) + \eta_-(\vartheta, \varphi)] \quad (4.46)$$

$$\delta\eta(\vartheta, \varphi) = \frac{1}{2}[\eta_+(\vartheta, \varphi) - \eta_-(\vartheta, \varphi)], \quad (4.47)$$

where $U(\vartheta, \varphi)$ is a shorthand, $\langle\bar{b}\rangle_n(\vartheta)$ is the average background contribution to the n th pair of measured $\pm$ signals, $2\langle\delta b\rangle_n(\vartheta)$ is the difference in the background contributions to the n th pair of measured $\pm$ signals, $\bar{\eta}(\vartheta, \varphi)$ is the average of the effective $\pm$ detection efficiencies and $2\delta\eta(\vartheta, \varphi)$ is the difference of the effective $\pm$ detection efficiencies. The

reader might find it helpful to note that (4.39) reduces to

$$\Delta_n(\vartheta, \varphi) = \frac{\cos(2\chi)\langle \ell S'_1 \rangle_n + \sin(2\chi)\langle \ell S_3 \rangle_n}{\langle \ell S_0 \rangle_n} \quad (4.48)$$

for the idealised case where the QWP and WP have no imperfections ($\tilde{\alpha} = \tilde{\beta} = \tilde{\gamma} = \tilde{\delta}_{\pm} = \tilde{\epsilon}_{\pm} = \tilde{\zeta}_{\pm} = 0$), the CAM has a constant background that has been perfectly subtracted ($\langle b_{\pm} \rangle_n(\vartheta) = 0$) and there is no effective detection efficiency imbalance ($\eta_+(\vartheta, \varphi) = \eta_-(\vartheta, \varphi)$).

4.3.1 A and B configurations and operating assumptions

We use our instrument in an “A configuration” and a “B configuration”, enabling us to overcome many artefacts by implementing a variant of Hug’s method of virtual enantiomers [125] via the ‘double deltas’ described below. In both configurations, we take the orientation of the WP to be fixed such that $\vartheta = -45^\circ + \delta\vartheta$ ($\vartheta_{\text{Anck}} = 221.27^\circ$), where $\delta\vartheta$ accounts for a possible angular miscalibration. In the A configuration, we take the QWP to be orientated such that $\chi_A = 45^\circ + \delta\chi$ ($\varphi_{\text{Imho},A} = 268.81^\circ$), where $\delta\chi$ accounts for another possible angular miscalibration. In the B configuration, we take the QWP to be rotated by a quarter turn such that $\chi_B = \chi_A + 90^\circ$ (we took $\varphi_{\text{Imho},B} = 358.81^\circ$), where little error should be introduced by considering exactly 90° as Imho is an extremely accurate and precise device. Note that the absolute QWP angles are $\varphi_A = \delta\vartheta + \delta\chi$ and $\varphi_B = 90^\circ + \delta\vartheta + \delta\chi$. In what follows, we suppress functional dependencies on ϑ .

The meaningful operation of our instrument relies on the following parameters and assumptions:

I The laser is sufficiently stable that $\ell(t) \approx 1$.

II The instrument is sufficiently well constructed and the optical activity of the sample sufficiently weak that $|S_1(t)/S_0(t)| \lesssim 10^{-2}$, $|S_2(t)/S_0(t)| \lesssim 10^{-3}$ and $|S_3(t)/S_0(t)| \lesssim 10^{-4}$.

- III** The QWP is of sufficiently high quality that $|\tilde{\alpha}| \lesssim 10^{-2}$, $|\tilde{\beta}| \lesssim 10^{-2}$ and $|\tilde{\gamma}| \lesssim 10^{-2}$.
- IV** The WP is of sufficiently high quality that $|\tilde{\delta}_{\pm}| \lesssim 10^{-2}$, $|\tilde{\epsilon}_{\pm}| \lesssim 10^{-2}$ and $|\tilde{\zeta}_{\pm}| \lesssim 10^{-2}$.
- V** The orientations of the QWP and WP are sufficiently well calibrated that $|\delta\chi| \lesssim 10^{-2}$ and $|\delta\vartheta| \lesssim 10^{-2}$.
- VI** The effective detection efficiencies are sufficiently good that $|\delta\eta(\varphi_A)/\bar{\eta}(\varphi_A)| \lesssim 10^{-2}$ and $|\delta\eta(\varphi_B)/\bar{\eta}(\varphi_B)| \lesssim 10^{-2}$. Note that $\vartheta = -45^\circ$ is an optimum choice in that it minimises contributions to $\delta\eta(\varphi_A)$ and $\eta(\varphi_B)$ due to an observed $\sim 10\%$ vertical/horizontal linear dichroism in the CAM.
- VII** The background subtraction is sufficiently good and the scattered light sufficiently intense that

$$2\langle\bar{b}\rangle_n/\bar{\eta}(\varphi_A)\langle\ell S_0\rangle_n \lesssim 10^{-3}, \quad 2\langle\bar{b}\rangle_n/\bar{\eta}(\varphi_B)\langle\ell S_0\rangle_n \lesssim 10^{-3}, \quad 2\langle\delta b\rangle_n/\bar{\eta}(\varphi_A)\langle\ell S_0\rangle_n \lesssim 10^{-4} \text{ and } 2\langle\delta b\rangle_n/\bar{\eta}(\varphi_B)\langle\ell S_0\rangle_n \lesssim 10^{-4}.$$

Neglecting terms of order 10^{-5} and smaller, it then follows from (4.39) that

$$\Delta_n(\varphi_A) = \Delta_{n,\text{background}}(\varphi_A) + \Delta_{n,\text{imbalance}}(\varphi_A) + \Delta_{n,\text{polarisation}}(\varphi_A) \quad (4.49)$$

$$\Delta_n(\varphi_B) = \Delta_{n,\text{background}}(\varphi_B) + \Delta_{n,\text{imbalance}}(\varphi_B) + \Delta_{n,\text{polarisation}}(\varphi_B) \quad (4.50)$$

with

$$\Delta_{n,\text{background}}(\varphi_A) \approx \frac{2\langle\delta b\rangle_n}{\bar{\eta}(\varphi_A)\langle\ell S_0\rangle_n}, \quad (4.51)$$

$$\Delta_{n,\text{imbalance}}(\varphi_A) \approx \frac{\delta\eta(\varphi_A)}{\bar{\eta}(\varphi_A)} \quad (4.52)$$

$$\begin{aligned} \Delta_{n,\text{polarisation}}(\varphi_A) \approx & -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ & + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \frac{\langle\ell S_1\rangle_n}{\langle\ell S_0\rangle_n} \\ & + [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] + \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \end{aligned} \quad (4.53)$$

for the A configuration and

$$\Delta_{n,\text{background}}(\varphi_B) \approx \frac{2\langle\delta b\rangle_n}{\bar{\eta}(\varphi_B)\langle\ell S_0\rangle_n}, \quad (4.54)$$

$$\Delta_{n,\text{imbalance}}(\varphi_B) \approx \frac{\delta\eta(\varphi_B)}{\bar{\eta}(\varphi_B)} \quad (4.55)$$

$$\begin{aligned} \Delta_{n,\text{polarisation}}(\varphi_B) \approx & -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ & + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \frac{\langle\ell S_1\rangle_n}{\langle\ell S_0\rangle_n} \\ & - [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] - \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \end{aligned} \quad (4.56)$$

for the B configuration. The reader might find it helpful to note that (4.49) and (4.50) reduce to

$$\Delta_n(\varphi_A) = \frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \quad (4.57)$$

$$\Delta_n(\varphi_B) = -\frac{\langle\ell S_3\rangle_n}{\langle\ell S_0\rangle_n} \quad (4.58)$$

for the idealised case where the QWP and WP have no imperfections ($\tilde{\alpha} = \tilde{\beta} = \tilde{\gamma} = \tilde{\delta}_\pm = \tilde{\epsilon}_\pm = \tilde{\zeta}_\pm = 0$), the CAM has a constant background that has been perfectly subtracted ($\langle b_\pm \rangle_n(\vartheta) = 0$) and there is no effective detection efficiency imbalance ($\eta_+(\vartheta, \varphi) = \eta_-(\vartheta, \varphi)$).

4.3.2 ‘Single deltas’

Suppose now that we take N_A exposures in the A configuration, giving N_A values of $\Delta_n(\varphi_A)$. The average of these is

$$\begin{aligned}\Delta(\varphi_A) &= \frac{1}{N_A} \sum_{n \in A} \Delta_n(\varphi_A) \\ &= \Delta_{\text{background}}(\varphi_A) + \Delta_{\text{imbalance}}(\varphi_A) + \Delta_{\text{polarisation}}(\varphi_A)\end{aligned}\quad (4.59)$$

with

$$\begin{aligned}\Delta_{\text{background}}(\varphi_A) &= \frac{1}{N_A} \sum_{n \in A} \Delta_{n,\text{background}}(\varphi_A) \\ &\approx \frac{2}{N_A \bar{\eta}(\varphi_A)} \sum_{n \in A} \frac{\langle \delta b \rangle_n}{\langle \ell S_0 \rangle_n},\end{aligned}\quad (4.60)$$

$$\begin{aligned}\Delta_{\text{imbalance}}(\varphi_A) &= \frac{1}{N_A} \sum_{n \in A} \Delta_{n,\text{imbalance}}(\varphi_A) \\ &\approx \frac{\delta \eta(\varphi_A)}{\bar{\eta}(\varphi_A)}\end{aligned}\quad (4.61)$$

$$\begin{aligned}\Delta_{\text{polarisation}}(\varphi_A) &= \frac{1}{N_A} \sum_{n \in A} \Delta_{n,\text{polarisation}}(\varphi_A) \\ &\approx -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ &\quad + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \frac{1}{N_A} \sum_{n \in A} \frac{\langle \ell S_1 \rangle_n}{\langle \ell S_0 \rangle_n} \\ &\quad + [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] + \frac{1}{N_A} \sum_{n \in A} \frac{\langle \ell S_3 \rangle_n}{\langle \ell S_0 \rangle_n}.\end{aligned}\quad (4.62)$$

Similarly, suppose we take N_B exposures in the B configuration, giving N_B values of $\Delta_n(\varphi_B)$. The average of these is

$$\begin{aligned}\Delta(\varphi_B) &= \frac{1}{N_B} \sum_{n \in B} \Delta_n(\varphi_B) \\ &= \Delta_{\text{background}}(\varphi_B) + \Delta_{\text{imbalance}}(\varphi_B) + \Delta_{\text{polarisation}}(\varphi_B)\end{aligned}\quad (4.63)$$

with

$$\begin{aligned}\Delta_{\text{background}}(\varphi_B) &= \frac{1}{N_B} \sum_{n \in B} \Delta_{n,\text{background}}(\varphi_B) \\ &\approx \frac{2}{N_B \bar{\eta}(\varphi_B)} \sum_{n \in B} \frac{\langle \delta b \rangle_n}{\langle \ell S_0 \rangle_n},\end{aligned}\tag{4.64}$$

$$\begin{aligned}\Delta_{\text{imbalance}}(\varphi_B) &= \frac{1}{N_B} \sum_{n \in B} \Delta_{n,\text{imbalance}}(\varphi_B) \\ &\approx \frac{\delta \eta(\varphi_B)}{\bar{\eta}(\varphi_B)}\end{aligned}\tag{4.65}$$

$$\begin{aligned}\Delta_{\text{polarisation}}(\varphi_B) &= \frac{1}{N_B} \sum_{n \in B} \Delta_{n,\text{polarisation}}(\varphi_B) \\ &\approx -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ &\quad + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \frac{1}{N_B} \sum_{n \in B} \frac{\langle \ell S_1 \rangle_n}{\langle \ell S_0 \rangle_n} \\ &\quad - [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] - \frac{1}{N_B} \sum_{n \in B} \frac{\langle \ell S_3 \rangle_n}{\langle \ell S_0 \rangle_n}.\end{aligned}\tag{4.66}$$

For a large number of exposures ($N_A \rightarrow \infty$ and $N_B \rightarrow \infty$) these results should tend towards

$$\Delta_{\text{background}}(\varphi_A) \approx 0, \quad (4.67)$$

$$\Delta_{\text{imbalance}}(\varphi_A) \approx \frac{\delta\eta(\varphi_A)}{\bar{\eta}(\varphi_A)}, \quad (4.68)$$

$$\begin{aligned} \Delta_{\text{polarisation}}(\varphi_A) \approx & -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ & + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \left\langle \frac{S_1}{S_0} \right\rangle_\infty \\ & + [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] + \left\langle \frac{S_3}{S_0} \right\rangle_\infty, \end{aligned} \quad (4.69)$$

$$\Delta_{\text{background}}(\varphi_B) \approx 0, \quad (4.70)$$

$$\Delta_{\text{imbalance}}(\varphi_B) \approx \frac{\delta\eta(\varphi_B)}{\bar{\eta}(\varphi_B)}, \quad (4.71)$$

$$\begin{aligned} \Delta_{\text{polarisation}}(\varphi_B) \approx & -(\alpha + \beta')(\delta'_+ + \delta'_-) + \frac{1}{2}(|\tilde{\delta}_+|^2 - |\tilde{\delta}_-|^2) + \frac{1}{2}(|\tilde{\epsilon}_+|^2 - |\tilde{\epsilon}_-|^2) \\ & + \frac{1}{2}(|\tilde{\zeta}_+|^2 - |\tilde{\zeta}_-|^2) - (\alpha' - \beta + \delta_+ - \delta_- + 2\delta\chi) \left\langle \frac{S_1}{S_0} \right\rangle_\infty \\ & - [\alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma'] - \left\langle \frac{S_3}{S_0} \right\rangle_\infty. \end{aligned} \quad (4.72)$$

We refer to $\Delta(\varphi_A)$ and $\Delta(\varphi_B)$ as ‘single deltas’ because they depend on differences of measured $\pm$ signals as seen in the numerator of (4.39) and to contrast them with the ‘double deltas’ and ‘triple deltas’ considered below.

4.3.3 ‘Double deltas’

We can eliminate many of the artefacts inherent to the ‘single delta’ values $\Delta(\varphi_A)$ and $\Delta(\varphi_B)$ by constructing the ‘double Delta’ value

$$\begin{aligned} \Delta\Delta &= \frac{1}{2}(\Delta(\varphi_A) - \Delta(\varphi_B)) \\ &= \Delta\Delta_{\text{circularity}} + \Delta\Delta_{\text{offset}} \end{aligned} \quad (4.73)$$

with

$$\Delta\Delta_{\text{circularity}} = \left\langle \frac{S_3}{S_0} \right\rangle_{\infty} \quad (4.74)$$

$$\Delta\Delta_{\text{offset}} = \alpha' + \beta - \alpha\gamma + (\beta - \delta_+ + \delta_- - 2\delta\chi)\gamma' + \frac{\delta\eta(\varphi_A)}{\bar{\eta}(\varphi_A)} - \frac{\delta\eta(\varphi_B)}{\bar{\eta}(\varphi_B)}, \quad (4.75)$$

where $\Delta\Delta_{\text{circularity}}$ is the degree of circularity of the scattered light and $\Delta\Delta_{\text{offset}}$ is an unwanted offset in our instrument, comprised of residual polarisation artefacts and effective detection efficiency imbalances. The ‘double delta’ notation and nomenclature alludes to the fact that $\Delta\Delta$ is essentially a ‘difference of differences’.

The value of the offset $\Delta\Delta_{\text{offset}}$ can be minimised by constructing the instrument carefully using high quality optical components and spatially integrating over as much of $\pm$ images as possible whilst ensuring we do not make the integration areas so large that we diminish the signal-to-noise ratio enough to violate the assumptions underpinning the meaningful operation of our instrument.

4.3.4 ‘Triple deltas’

A ‘double delta’ $\Delta\Delta$ for a given sample can only be compared directly to a theoretically predicted circular intensity differential Δ if the optical rotation of the incident light is negligible, if the sample is 100% enantiopure and if the instrumental offset $\Delta\Delta_{\text{offset}}$ is zero. These requirements can never be met exactly.

If, however, we have a *pair* of ‘double deltas’ $\Delta\Delta(S)$ and $\Delta\Delta(R)$ for *both* enantiomers of a chiral molecule, we can correct for optical rotation, racemisation and the instrumental offset $\Delta\Delta_{\text{offset}}$ via the construction of ‘triple deltas’ $\Delta\Delta\Delta(S) = -\Delta\Delta\Delta(R)$ as follows. The ‘triple delta’ notation and nomenclature alludes to the fact that $\Delta\Delta\Delta(S) = -\Delta\Delta\Delta(R)$ are essentially ‘differences of differences of differences’.

We take the ‘double deltas’ $\Delta\Delta(S)$ and $\Delta\Delta(R)$ to be related to the ‘triple deltas’

$\Delta\Delta\Delta(S) = -\Delta\Delta\Delta(R)$ as

$$\Delta\Delta(S) = \frac{ee(S)}{q(S)}\Delta\Delta\Delta(S) + \Delta\Delta_{\text{offset}} \quad (4.76)$$

$$\Delta\Delta(R) = \frac{ee(R)}{q(R)}\Delta\Delta\Delta(R) + \Delta\Delta_{\text{offset}} \quad (4.77)$$

where $ee(S)$ and $ee(R)$ are the enantiomeric excesses of the sample and $q(S)$ and $q(R)$ account for the introduction of isotropic scattering via optical rotation. Assuming the optical rotation to be small, basic isotropic scattering theory (as seen in section 2.3) gives

$$q(S) \approx 1 + \frac{1}{12}\{1 + \cos[2\theta^i(S)]\}[45N\chi_T k_B T(\alpha^2/\beta^2) + 1] \quad (4.78)$$

$$q(R) \approx 1 + \frac{1}{12}\{1 + \cos[2\theta^i(R)]\}[45N\chi_T k_B T(\alpha^2/\beta^2) + 1] \quad (4.79)$$

for neat samples, where θ^i is the incident polarisation azimuth, N is the molecular number density, χ_T is the isothermal compressibility, T is the temperature, α^2 is the isotropic rotational invariant of an individual molecule and β^2 is the anisotropic rotational invariant. Simple algebra reveals that

$$\Delta\Delta\Delta(S) = f(\Delta\Delta(S) - \overline{\Delta\Delta}) \quad (4.80)$$

$$\Delta\Delta\Delta(R) = f(\Delta\Delta(R) - \overline{\Delta\Delta}) \quad (4.81)$$

with

$$f = \frac{2q(S)q(R)}{ee(S)q(R) + ee(R)q(S)} \quad (4.82)$$

$$\overline{\Delta\Delta} = \frac{1}{2}(\Delta\Delta(S) + \Delta\Delta(R)), \quad (4.83)$$

where the magnitude rescaling factor f accounts for the effects of optical rotation and racemisation and $\overline{\Delta\Delta}$ is the average of the ‘double deltas’ $\Delta\Delta(S)$ and $\Delta\Delta(R)$, sub-

tracted to remove the instrumental offset $\Delta\Delta_{\text{offset}}$. Note the equivalent expressions

$$\Delta\Delta\Delta(S) = \frac{1}{2}f(\Delta\Delta(S) - \Delta\Delta(R)) \quad (4.84)$$

$$\Delta\Delta\Delta(R) = \frac{1}{2}f(\Delta\Delta(R) - \Delta\Delta(S)), \quad (4.85)$$

which show explicitly that $\Delta\Delta\Delta(S)$ and $\Delta\Delta\Delta(R)$ have equal magnitudes but opposite signs, as they should.

The ‘triple deltas’ $\Delta\Delta\Delta(S) = -\Delta\Delta\Delta(R)$ represent our most robust experimental estimates of the theoretically predicted circular intensity differentials $\Delta(S) = -\Delta(R)$.

Note that the offset $\Delta\Delta_{\text{offset}}$ can be extracted using the somewhat cumbersome expression

$$\Delta\Delta_{\text{offset}} = \frac{ee(R)q(S)\Delta\Delta(S) + ee(S)q(R)\Delta\Delta(R)}{2[ee(S)q(R) + ee(R)q(S)]}, \quad (4.86)$$

which reduces to the average of the ‘double deltas’ $\Delta\Delta(S)$ and $\Delta\Delta(R)$ for the special case where the mirror-image samples have the same magnitudes of enantiopurity ($ee(S) = ee(R)$) and the same magnitudes of optical rotation ($q(S) = q(R)$).

4.4 Summary and outlook

We have presented an overview of our dedicated RayOA instrument, including a detailed theoretical model of our high-precision detection train. Our model can be refined further by including spatial variations in the Stokes parameters of the scattered light, angular variations of the QWP and WP imperfection parameters and polarisation sensitivity of the CAM.

Chapter 5

Measurements of RayOA

5.1 Introduction

In this chapter, we present measurements of RayOA circular intensity differentials for small chiral molecules and viruses, obtained following the strategy outlined in chapter 3 using the dedicated RayOA instrument described in chapter 4.

5.2 Small chiral molecules

In this section, we present measurements of RayOA circular intensity differentials for the enantiomers of α -pinene. Each of our two samples consisted of 2 mL in neat liquid form (Merck analytical standards 80599, 80605). These results constitute the first-ever experimental observation of RayOA for small chiral molecules and were the focus of a high-profile (front cover) publication [121].

We focus in what follows on a single pair of representative measurement runs for the sake of clarity. Repeated measurement runs gave consistent results.

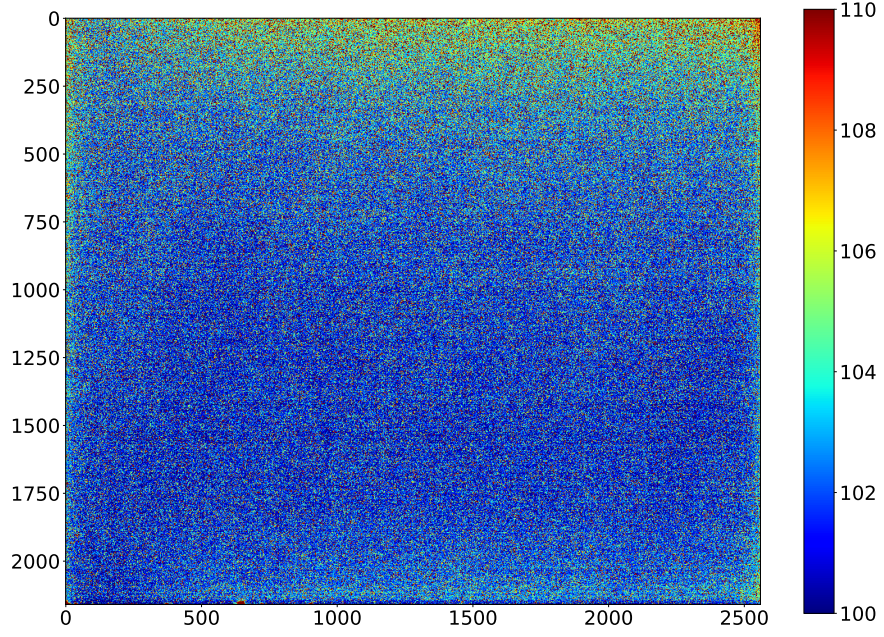
5.2.1 Instrument control

We wrote a comprehensive Python script that controls our instrument and effectively automates data-acquisition. All the scientific instruments that required fine control

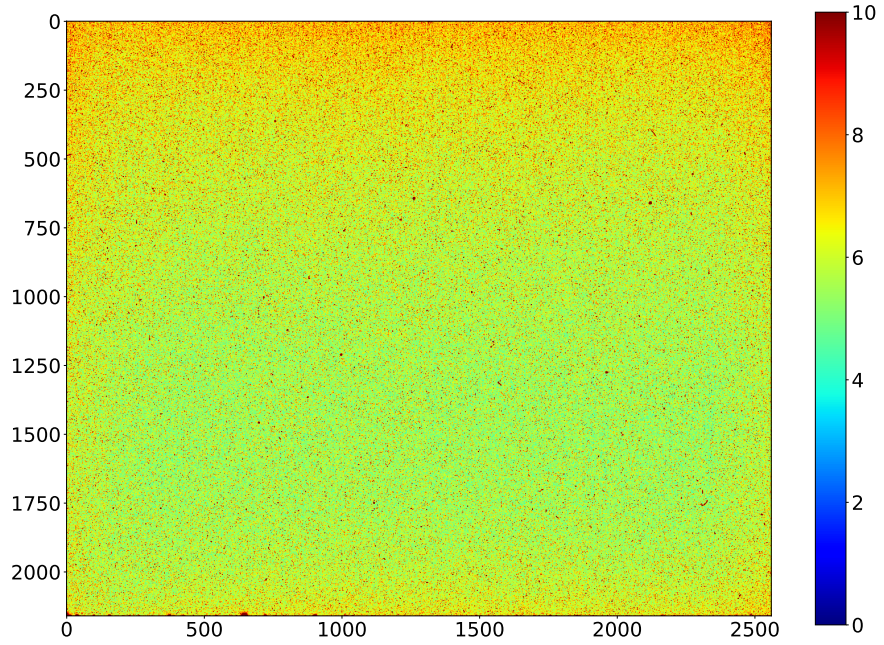
were connected to the lab computer via USB and controlled via this Python script. This included the USB power meter, the “Imho” and “Anck” motorised rotation mounts that control the orientation of the quarter wave-plate (QWP) and the orientation of the Wollaston prism (WP) and finally the sCMOS camera (CAM).

5.2.2 Camera background

Initially, 100 background images were collected with the laser turned off. These were then averaged to obtain a single mean background image, seen in Fig. 5.1a. Those background images were captured with the same $\Delta t = 30$ s exposure time as the sample images and with the camera sensor cooled to 0° C. Additionally, shown in Fig. 5.1b, a standard deviation image was created from all the background images to demonstrate the variability of pixel values over time. The mean background image has a mean pixel value of 107.57 counts and the standard deviation image has a mean of 6.18 counts.



(a) Mean background image on a per-pixel basis.



(b) Standard deviation background image on a per-pixel basis.

Figure 5.1: Mean and standard deviation background images obtained on a per-pixel basis from 100 dark images, each with an $\Delta t = 30$ s exposure time. The units of the horizontal and vertical axes are number of pixels and the units of the colour bars are 16-bit pixel counts.

5.2.3 Data acquisition

A single measurement run on a given sample required the capture of multiple exposures at the maximum available exposure time that the CAM allowed ($\Delta t = 30$ s). The exposures were captured at a 16-bit depth for the maximum amount of intensity variation to be resolved. In order to optimally distribute any laser fluctuations or drifting throughout our measurements, we were alternating the QWP angle every 5 images between the two orientations of interest, realising the A and B configurations. A typical measurement run consisted of $N_A + N_B = 1200$ exposures ($N_A = N_B = 600$ exposures per configuration), giving a total data acquisition time of ~ 11 hours.

During a measurement run we collected two sets of data; images of the scattered light are collected with the CAM and saved as TIFF files and laser optical powers are collected with our Thorlabs optical power meter and saved in a dedicated Microsoft Excel file. Both happen automatically via our python script that executes all the commands. Before the measurement run starts, the CAM air-cooler activates and cools the sensor to 0°C and makes sure it stays at that temperature. For each $\Delta t = 30$ s exposure, power meter measurements were taken roughly every 3 s for a total of 8 measurements that were then averaged to generate a single representative optical power value. All these power values were saved in a Microsoft Excel file automatically via our python script.

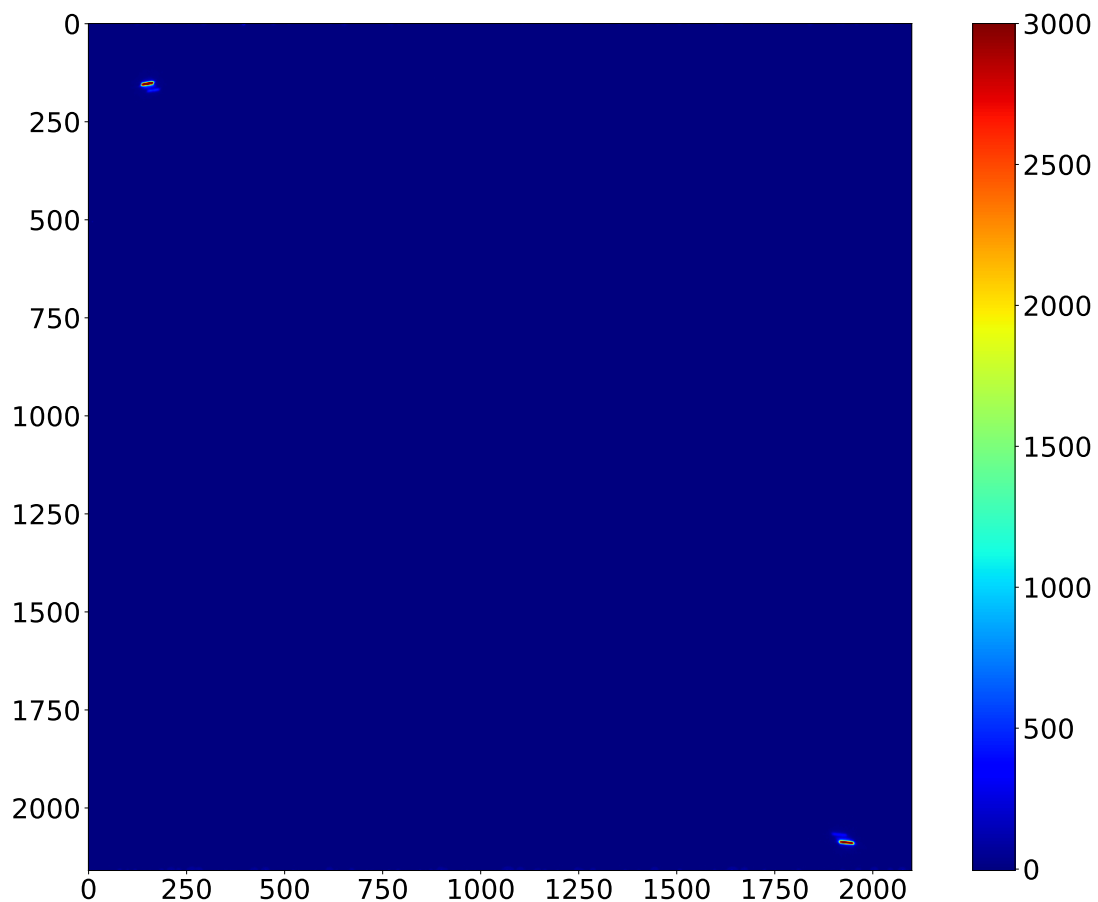


Figure 5.2: Raw, cropped scattered light image of $(1R, 5R)$ - α -pinene. The two spots have been tightly focused in small regions to minimise errors and maximise the SNR. The units of the horizontal and vertical axes are number of pixels and the units of the colour bars are 16-bit pixel counts. Image dimensions: 2160×2100 pixels.

5.2.4 Laser optical power analysis

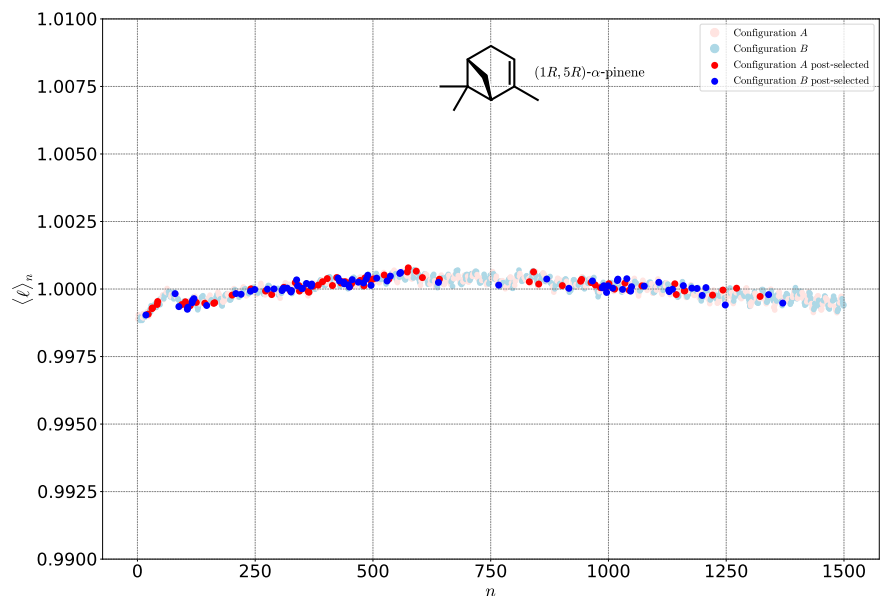
For a given measurement run on a given sample, the first step was to check the power meter data to get an understanding of laser power fluctuations. The measurement of the laser power occurs right after the laser using a half-wave plate and a 50/50 beam-splitter where the power meter was placed in one output of the beam splitter and the other output leads to the sample.

We define the following function:

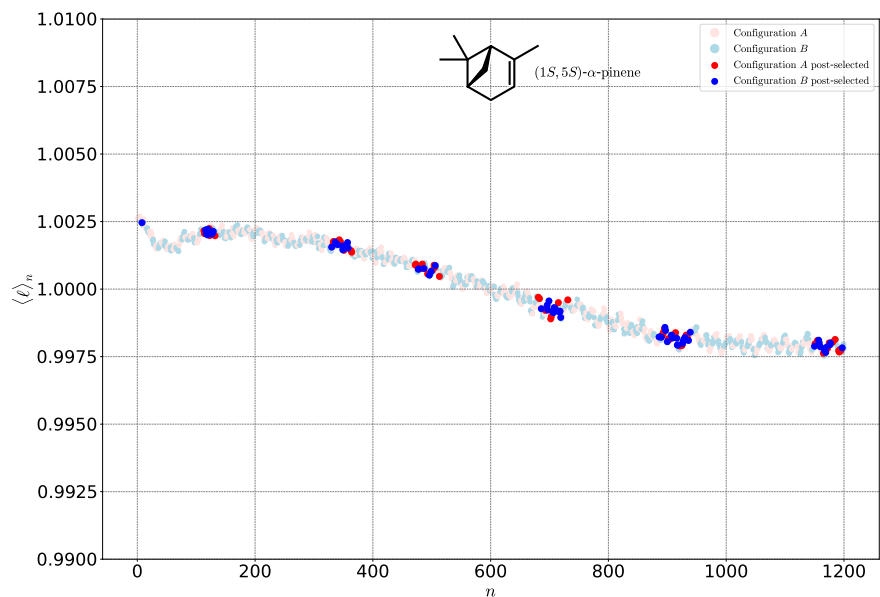
$$\langle \ell \rangle_n = \frac{\langle P \rangle_n}{\frac{1}{N_A + N_B} \sum_{n=1}^{N_A + N_B} \langle P \rangle_n}, \quad (5.1)$$

where $\langle P \rangle_n$ is the raw power measurement for the n th exposure and $\langle \ell \rangle_n$ is the power measurement for the n th exposure normalised by the mean power measurement.

In Fig. 5.3a and Fig. 5.3b, we see scatter plots of $\langle \ell \rangle_n$ for our representative measurement runs on the enantiomers of α -pinene, with our instrument alternating between A (red) and B (blue) configurations every 5 exposures. The laser manufacturer, CrystaLaser, quoted us a $< 0.25\%$ power output fluctuation over any 24-hour window of continuous operation. Our $\langle \ell \rangle_n$ plots confirm this, with a standard deviation $\sigma = 0.16\%$ for our measurement run on the $(1S, 5S)$ - α -pinene sample and $\sigma = 0.037\%$ for our final measurement run on the $(1R, 5R)$ - α -pinene sample. This confirms the validity of operating assumption **I** ($\ell(t) \approx 1$) described in chapter 4.



(a) Normalised laser power $\langle \ell \rangle_n$ versus exposure number n for a measurement run on (1R,5R)- α -pinene.



(b) Normalised laser power $\langle \ell \rangle_n$ versus exposure number n for a measurement run on (1S,5S)- α -pinene.

Figure 5.3: Scatter plots of the normalised laser power $\langle \ell \rangle_n$ versus exposure number n for representative measurement runs on the enantiomers of α -pinene. Red and blue correspond to the A and B configurations of our instrument, with post-selected data points highlighted in vivid colours and the remaining data points rendered in misty colours.

5.2.5 Noise reduction

The mean background image was subtracted from every exposure image to remove the background on a per-pixel basis, thus tackling the spatial noise of the CAM sensor. This spatial noise is a broad category of sensor noise containing offset spatial variation, column level gain variation, dark signal non-uniformity etc. The common characteristic of all these noise sources is that they stay relatively constant over time but vary spatially on the sensor. As a result, they do not “average away” if we collect multiple exposures and require instead this background subtraction to tackle effectively.

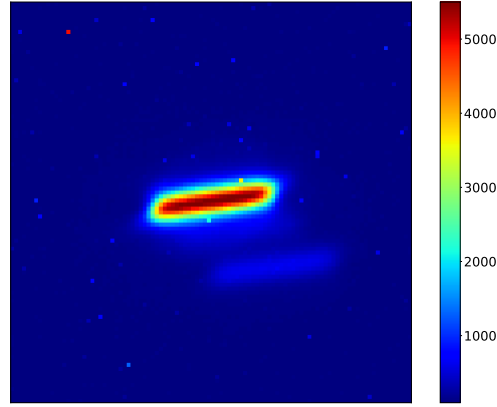
All exposure images were then cropped to exclude any edges that are not used in the analysis to reduce the computational burden and improve analysis time. The median filter function with a kernel size of 3×3 from the `scipy.ndimage` library was then applied to all exposure images to remove any remaining “salt and pepper” noise and for “hot pixel” correction. This is a non-linear filter function that is used routinely for these purposes [126–128] as it smooths out the images while at the same time preserving the underlying “crispness” of the signal much better than other linear filters (this is called edge-preservation in image processing terminology). This median filter along with taking multiple exposures, helps tackle the temporal noise of the CAM sensor that stays relatively constant spatially on the sensor but varies over time. Types of this temporal noise are dark current noise, transfer noise and various forms of electronic noise like RTS (Random Telegraph Signal) noise, $1/f$ noise etc.

In Fig. 5.4, we can see a zoomed in region of 100×100 pixels centred around the + signal image that demonstrates how the background subtraction and median filtering modifies the image in stages. Note the presence of a diagonally displaced “ghost” image of the laser beam with intensity of $\sim 10\%$ of the scattered image itself. Our current understanding is that this “ghost” image comes from a small but non-trivial amount of fluorescence generated in the sample. This fluorescence is Stokes-shifted with respect to the incident laser beam and that is why it is diagonally shifted as the Wollaston prism in the scattering path is dispersive and can cause such slight shifts.

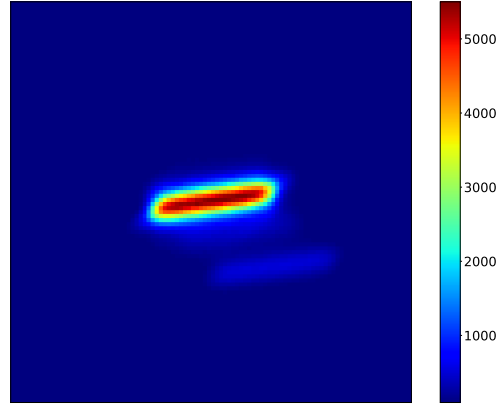
All further actions in the analysis process, like pixel summation to calculate inten-

Chapter 5. Measurements of RayOA

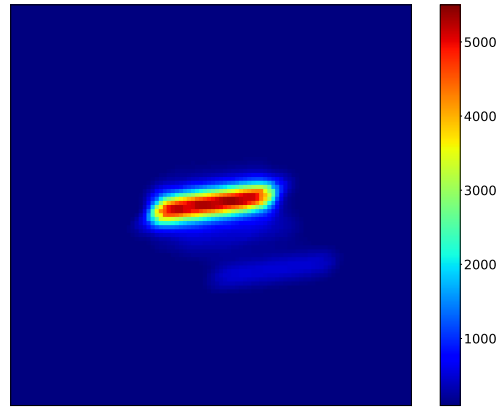
sities, are applied on those 100×100 pixel areas for each spot individually.



(a) Average raw image.



(b) Average raw image with background subtraction.

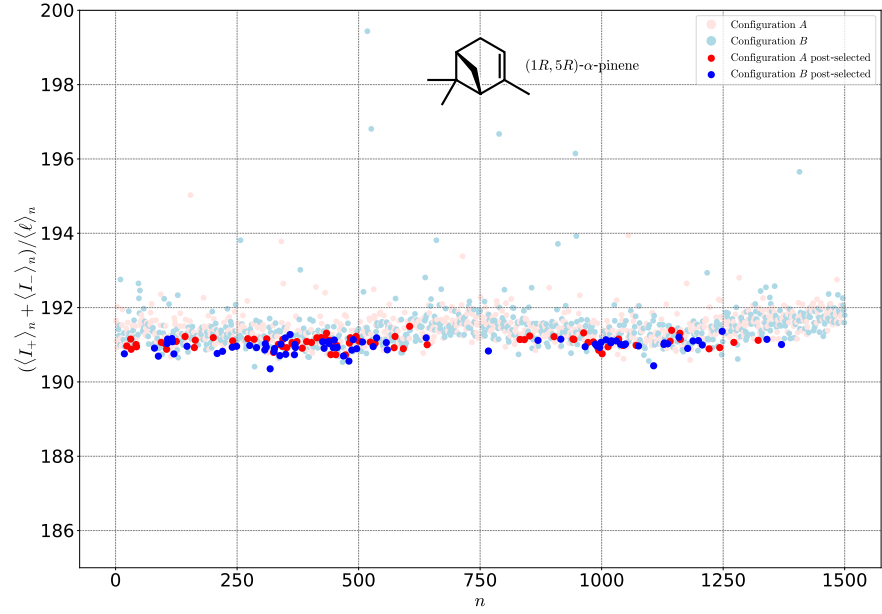


(c) Average raw image with background subtraction and median filter applied.

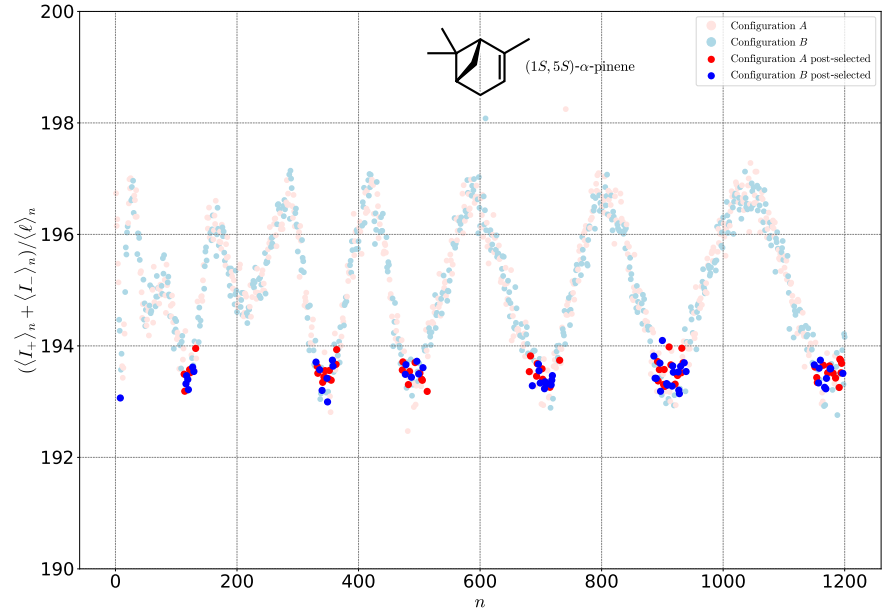
Figure 5.4: Averaged images of the + signal at three different stages of processing; raw data, background subtracted data on a per-pixel basis, and background subtracted data with additional median filtering with a 3×3 kernel. Images shown are 100×100 pixels with the instrument in the *A* configuration for (1*S*, 5*S*)- α -pinene

5.2.6 Post selection

We perform a post selection of exposures where we target those with the lowest total scattered intensity. The samples do tend to contain dust or other small impurities due to imperfect preparation and these contaminants can only scatter more light by definition while the “pure” Rayleigh-scattered light from our sample forms a scattering intensity “floor”. Complementary to that, we also want to avoid the very lowest total intensity images due to a potential momentary block of the laser beam due to dust floating in the air or something else. As a result, the heuristic we opted for was to choose the 10% of images that lie between the bottom 5th and 15th percentile in terms of total light scattering. This heuristic works well because it filters out the majority of scattered signal coming from impurities while leaving enough “surviving” images to work with and reduce uncertainties by $1/\sqrt{N}$. Such techniques, where the majority of high total intensity scattering data is discarded and only a narrow sliver of the lowest intensity scattering data is retained, are commonly used in the quasi-elastic light scattering literature like the seminal Zhang et al. paper [129] on the depolarisation ratio of water.



(a) Results for measurement run on (1R, 5R)-α-pinene.



(b) Results for measurement run on (1S, 5S)-α-pinene.

Figure 5.5: Total measured signal $((I_+)_n + (I_-)_n) / (\ell)_n$ versus exposure number n for measurement runs on the enantiomers of α -pinene, with normalisation by $(\ell)_n$ to correct for laser fluctuations. The oscillatory variation of $\sim 2\text{-}3\%$ seen for the measurement run on (1S, 5S) might be due to modulation of the servo mechanism in the laser responsible for optical power output stability. However, this is largely mitigated by the post selection procedure.

5.2.7 Masks

The background subtraction and median filter smoothing work reliably well but they are not perfect. On a per pixel basis, there are pixels that end up with a slight negative value after the background subtraction and there can be clustered hot-spots that can still survive the median filtering. As a result, we cannot just sum over all pixels in a given image to calculate intensities as that leads to accumulated errors that will skew our measurement results in the 10^{-3} - 10^{-5} range.

The way we opted to tackle this, and the fluorescence “ghost” evident in Fig. 5.4, was by creating masks for our images (one for the + signal image and one for the – signal image) with the same dimensions, whose values are continuous in the range $[0, 1]$ that are multiplied by our images on an pixel-by-pixel basis. This creates a “weighting” effect where pixels far from the signal do not contribute to the intensity sum where pixels near the centre of the beam that have high intensity contribute more. To create these masks, we take all our images after background subtraction, median filtering and total intensity post-selection and average them to create one mean image (including images from both QWP angles). We then slice a 100×100 region of interest (ROI) centered on the ordinary spot. We then calculate the maximum value pixel and the minimum value pixel and their difference represents the range of values in this ROI. We are then free to select a threshold percentage $x\%$ of that range where every pixel in the ROI that has a value equal or larger than that will be marked as 1 in the mask and if below then 0. Doing this for different values of x and creating a binary plot of the results, we clearly see that with an increasing x , we get a larger region in the mask that starts to resemble the tic-tac shape of our actual beam and is of a contiguous nature. However, once you go above 90%, the shape starts to deform and starts capturing other far-away pixels in a non-contiguous way. Therefore, we generate masks for the percentage range 80% – 90% with a step of 1% and then average those to create one final mask. The same process is then employed on the extraordinary spot.

We did this process for both of the α -pinene samples and then we averaged the masks of these two samples into a final set of two masks to be used for both.

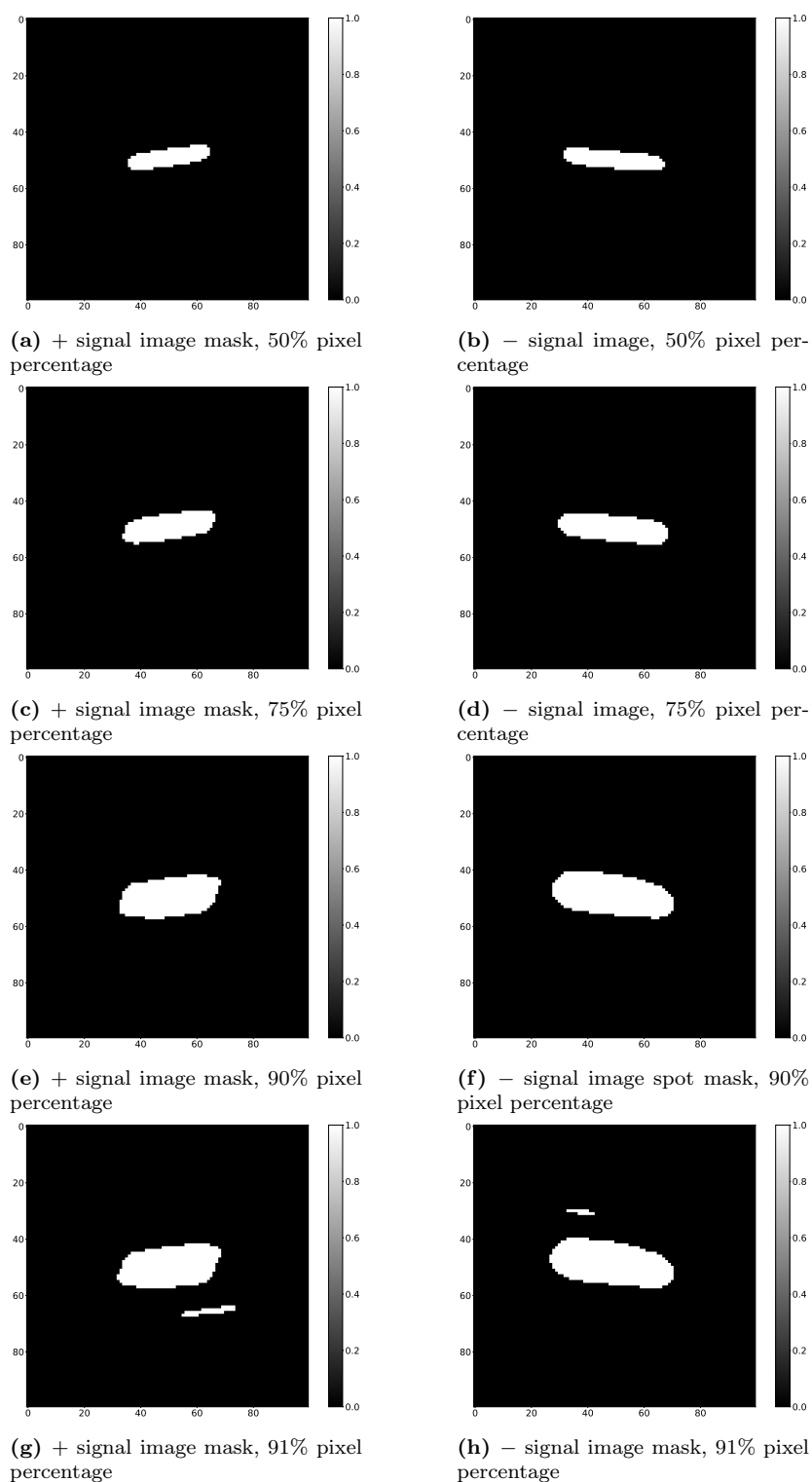


Figure 5.6: A selection of pixel percentage masks for a measurement run on $(1S,5S)\text{-}\alpha\text{-pinene}$. The larger the pixel percentage, the larger the number of pixels that are included in the calculation of the $\pm$ signals. For pixel percentages over 90%, the masks form a non-contiguous shape that includes unwanted contributions due to the fluorescence “ghost”.

A helpful flow chart can be seen in Fig.5.7 that summarises the process of our analysis from importing raw measurements to refining them for final calculations.

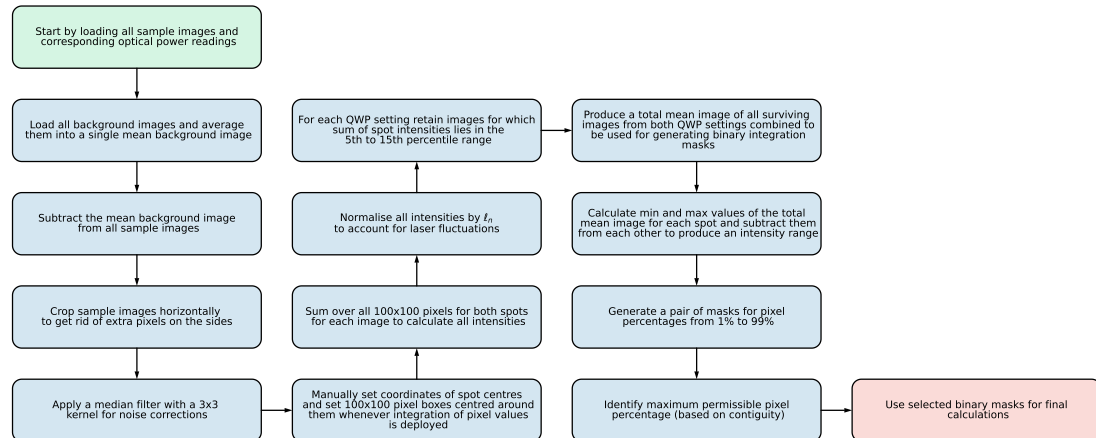


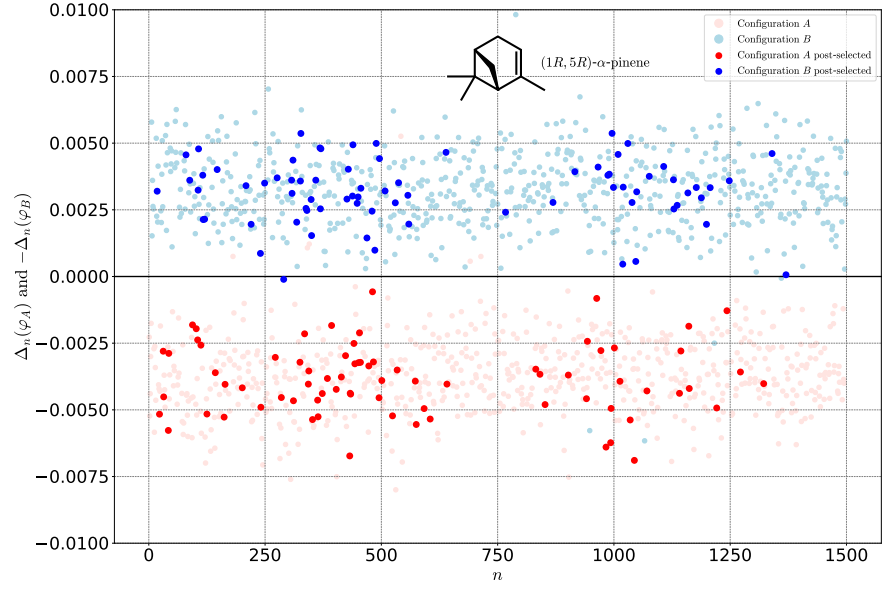
Figure 5.7: Flow chart of analysis pipeline from importing raw data (green) to final calculations (red).

5.2.8 ‘Single deltas’

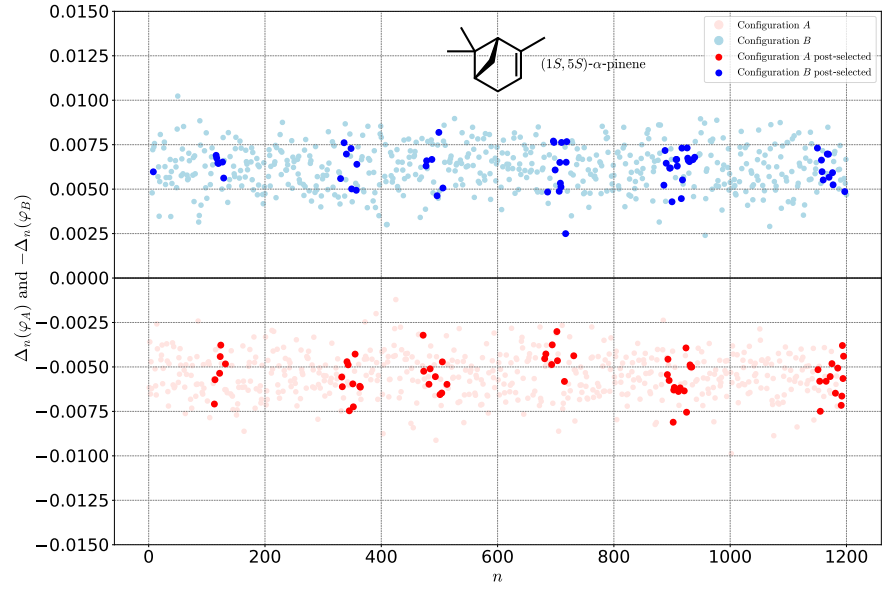
After all these steps of data processing, eliminating noise, post-selecting data points etc, we are now in a position to extract the ‘single delta’ values for the measurement runs on our α -pinene enantiomers.

In Fig. 5.8, we have plotted the $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ values versus exposure number n for both measurement runs on the enantiomers of α -pinene. Note that the ‘double delta’ $\Delta\Delta$ values are given by the average of these plots, as indicated in (4.73).

Chapter 5. Measurements of RayOA



(a) Results for measurement run on (1R, 5R)-α-pinene.



(b) Results for measurement run on (1S, 5S)-α-pinene.

Figure 5.8: Plots of $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus exposure number n . Red and blue correspond to the A and B configurations of our instrument, with post-selected data points highlighted in vivid colours and the remaining data points rendered in misty colours.

5.2.9 ‘Double deltas’

In Fig. 5.9, we have plotted all the ‘double delta’ $\Delta\Delta$ values as a function of the pixel percentage used in the masks for both measurement runs on the enantiomers of α -pinene. As the pixel percentage gets larger, the $\Delta\Delta$ values of both enantiomers tend towards their predicted value from the quantum chemistry calculations as more of the Rayleigh scattered light is included in the measurement up to a point. As explained above in the masks section, when the pixel percentage goes above 90%, light due to fluorescence starts to be picked up by the masks (appearing as a non-contiguous shape in Fig. 5.6 and that affects the delicate balance of this measurement. We have therefore opted to use the 85%-86% range of pixel percentage for our final results as this sets the offset of our instrument to zero as shown in Fig. 5.10. Note, however, that any choice in the 80% and 90% range gives the same final results, as the ‘triple delta’ values tend towards a limit as shown in Fig. 5.11.

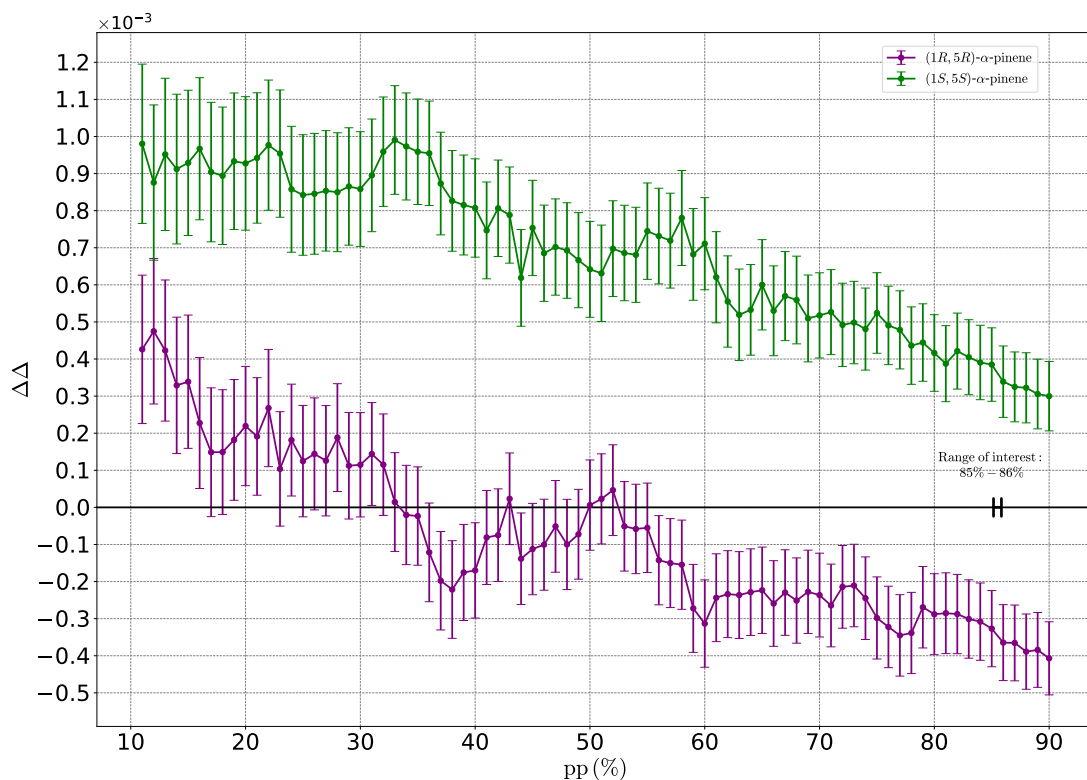


Figure 5.9: ‘Double deltas’ $\Delta\Delta$ versus pixel percentage for a pair of measurement runs on the enantiomers of α -pinene. Our final measurements come from the 85% – 86% range of interest as labelled. Note that average of the $\Delta\Delta$ values in this range is essentially zero, corresponding to a vanishing instrumental offset $\Delta\Delta_{\text{offset}}$.

5.2.10 ‘Triple deltas’

Let us now consider the determination of the magnitude rescaling factor f , needed to construct our ‘triple delta’ values $\Delta\Delta\Delta(1S, 5S) = -\Delta\Delta\Delta(1R, 5R)$ for comparison with our theoretically predicted circular intensity differentials $\Delta(1S, 5S) = -\Delta(1R, 5R)$ as described in section 4.3.4 of chapter 4.

For enantiopure samples, we would expect the optical rotation angles of the incident

light to be

$$\begin{aligned}\Delta\theta(1S, 5S) &= [\Delta\theta]_D(1S, 5S)l\rho(\lambda_D/\lambda)^2 \\ &= (-5.332 \pm 0.022)^\circ\end{aligned}\tag{5.2}$$

$$\begin{aligned}\Delta\theta(1R, 5R) &= [\Delta\theta]_D(1R, 5R)l\rho(\lambda_D/\lambda)^2 \\ &= (+5.332 \pm 0.022)^\circ,\end{aligned}\tag{5.3}$$

where $[\Delta\theta]_D(1S, 5S) = -[\Delta\theta]_D(1R, 5R)$ are the specific rotations of the enantiomers of α -pinene at the sodium D line, $l = (0.1000 \pm 0.0001)$ dm is the internal path length of the cuvettes, $\rho = (0.8580 \pm 0.0005)$ g cm⁻³ is the mass density of α -pinene and we have used a simple wavelength scaling to convert from the sodium D wavelength $\lambda_D = (589 \pm 1)$ nm to our chosen wavelength $\lambda = (532.0 \pm 0.5)$ nm. On the 27th of June 2025 we constructed a simple polarimeter to measure the actual optical rotation angles. The (1*S*,5*S*)- α -pinene and (1*R*,5*R*)- α -pinene samples were placed between two crossed linear polarisers (Thor Labs LPVISC-100A) and illuminated using a 0.9 mW compact laser module with wavelength 532 nm (Thor Labs CPS532-C2), the orientation of the second linear polariser being precisely controlled using the “Imho” motorised rotation mount. Transmitted power measurements were made using the USB power meter. The measured optical rotation angles are

$$\Delta\theta'(1S, 5S) = (-5.14 \pm 0.11)^\circ\tag{5.4}$$

$$\Delta\theta'(1R, 5R) = (+5.26 \pm 0.11)^\circ,\tag{5.5}$$

which reveals that the enantiomeric excesses are

$$\begin{aligned} ee(1S, 5S) &= \frac{\Delta\theta'(1S, 5S)}{\Delta\theta(1S, 5S)} \\ &= (96.4 \pm 2.1)\% \end{aligned} \quad (5.6)$$

$$\begin{aligned} ee(1R, 5R) &= \frac{\Delta\theta'(1R, 5R)}{\Delta\theta(1R, 5R)} \\ &= (98.6 \pm 2.1)\%. \end{aligned} \quad (5.7)$$

It is reasonable that $ee(1S, 5S)$ is smaller than $ee(1R, 5R)$ as we illuminated the $(1S, 5S)$ sample for many hours more than the $(1R, 5R)$ sample during the construction and calibration of our instrument, causing more thermal racemisation. We note also that the polarisation azimuths of the incident light in the scattering volumes are

$$\begin{aligned} \theta^i(1S, 5S) &= \theta^i + \Delta\theta'(1S, 5S)/2 \\ &= (87.43 \pm 0.26)^\circ \end{aligned} \quad (5.8)$$

$$\begin{aligned} \theta^i(1R, 5R) &= \theta^i + \Delta\theta'(1R, 5R)/2 \\ &= (92.63 \pm 0.26)^\circ, \end{aligned} \quad (5.9)$$

where $\theta^i = (90.00 \pm 0.25)^\circ$ is the polarisation azimuth of the incident light before entering the samples and we take the scattering volumes to be located in the middles of the cuvettes. The optical rotation correction factors from (4.78) and (4.79) are

$$\begin{aligned} q(1S, 5S) &= 1 + \frac{1}{12}\{1 + \cos[2\theta^i(1S, 5S)]\}[45N\chi_T k_B T(\alpha^2/\beta^2) + 1] \\ &= 1.0093 \pm 0.0026 \end{aligned} \quad (5.10)$$

$$\begin{aligned} q(1R, 5R) &= 1 + \frac{1}{12}\{1 + \cos[2\theta^i(1R, 5R)]\}[45N\chi_T k_B T(\alpha^2/\beta^2) + 1] \\ &= 1.0097 \pm 0.0027 \end{aligned} \quad (5.11)$$

to leading order, where $N = (3.790 \pm 0.005) \times 10^{27} \text{ m}^{-3}$ is the molecular number density of α -pinene, $\chi_T = (7.750 \pm 0.005) \times 10^{-10} \text{ Pa}^{-1}$ is the isothermal compressibility of

α -pinene, $T = (293 \pm 10)$ K is the temperature of the illuminated samples and $\alpha^2/\beta^2 = 50 \pm 10$ is a ratio of isotropic to anisotropic rotational invariants for α -pinene, estimated using Gaussian 09.

Putting the above together, we find from (4.82) that the magnitude rescaling factor is

$$\begin{aligned} f &= \frac{2q(1S, 5S)q(1R, 5R)}{ee(1S, 5S)q(1R, 5R) + ee(1R, 5R)q(1S, 5S)} \\ &= 1.035 \pm 0.016. \end{aligned} \tag{5.12}$$

showing that racemisation and optical rotation distort our results by nearly 4%.

Shown in Fig. 5.10 is a plot of the instrumental offset $\Delta\Delta_{\text{offset}}$ versus mask pixel percentage, calculated using ‘double deltas’ according to (4.86) with the enantiomeric excesses $ee(1S, 5S)$ and $ee(1R, 5R)$ and optical rotation correction factors $q(1S, 5S)$ and $q(1R, 5R)$ as determined above. The plot shows that the value of $\Delta\Delta_{\text{offset}}$ can be tuned to zero within error bars by choosing a mask pixel percentage of 85 – 86%.

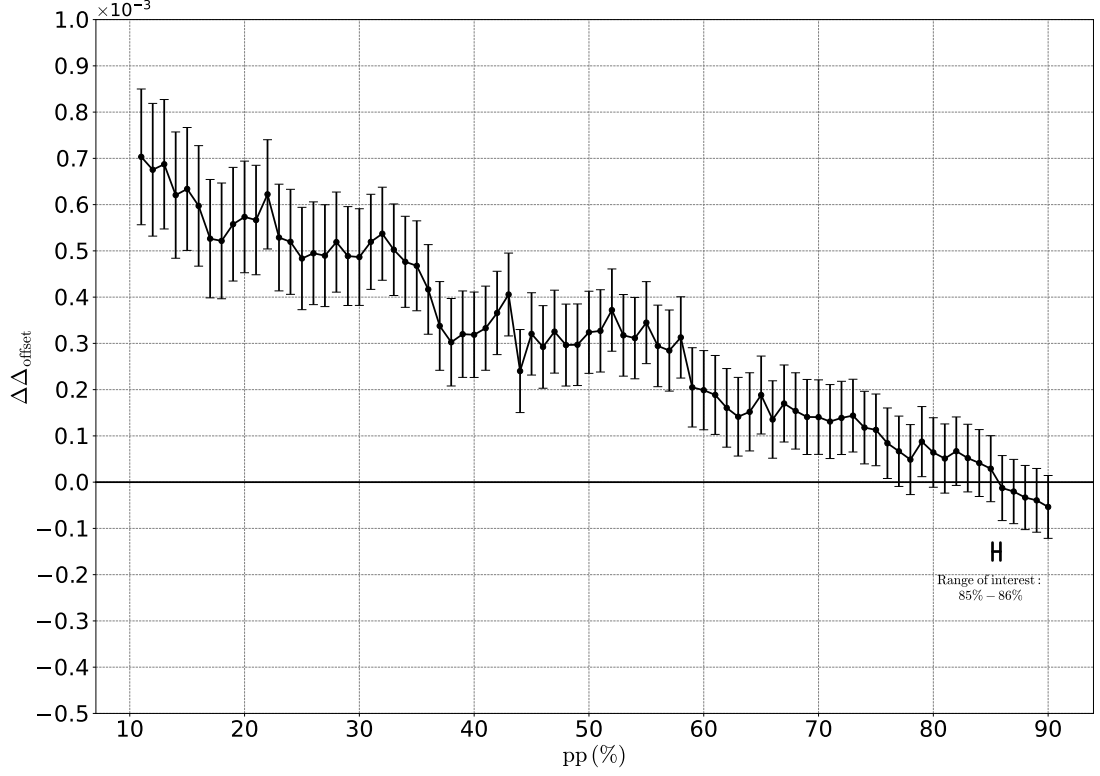


Figure 5.10: Instrumental offset $\Delta\Delta_{\text{offset}}$ versus mask pixel percentage.

Shown in Fig. 5.11 are plots of the ‘triple deltas’ $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ versus mask pixel percentage, calculated using ‘double deltas’ according to (4.84) and (4.85) with the f correction factor as determined above. These plots confirm that $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ tend towards limits as the pixel percentage is increased towards the choice of 85 – 86% that fixes the zero of our instrument. Based on this, we take our final results for the pair of measurement runs under consideration to be

$$\Delta\Delta\Delta(1S, 5S) = (+3.6 \pm 0.7) \times 10^{-4} \quad (5.13)$$

$$\Delta\Delta\Delta(1R, 5R) = (-3.6 \pm 0.7) \times 10^{-4}. \quad (5.14)$$

These values are plotted in Fig. 5.12 in comparison with our quantum-chemical predictions from chapter 4, where it can be seen that our measured and predicted values are in excellent agreement. Evidently, measurements of RayOA circular intensity differen-

tials at a single wavelength ($\lambda = 532\text{nm}$) can be used to correctly assign the absolute configuration of small chiral molecules like α -pinene [14].

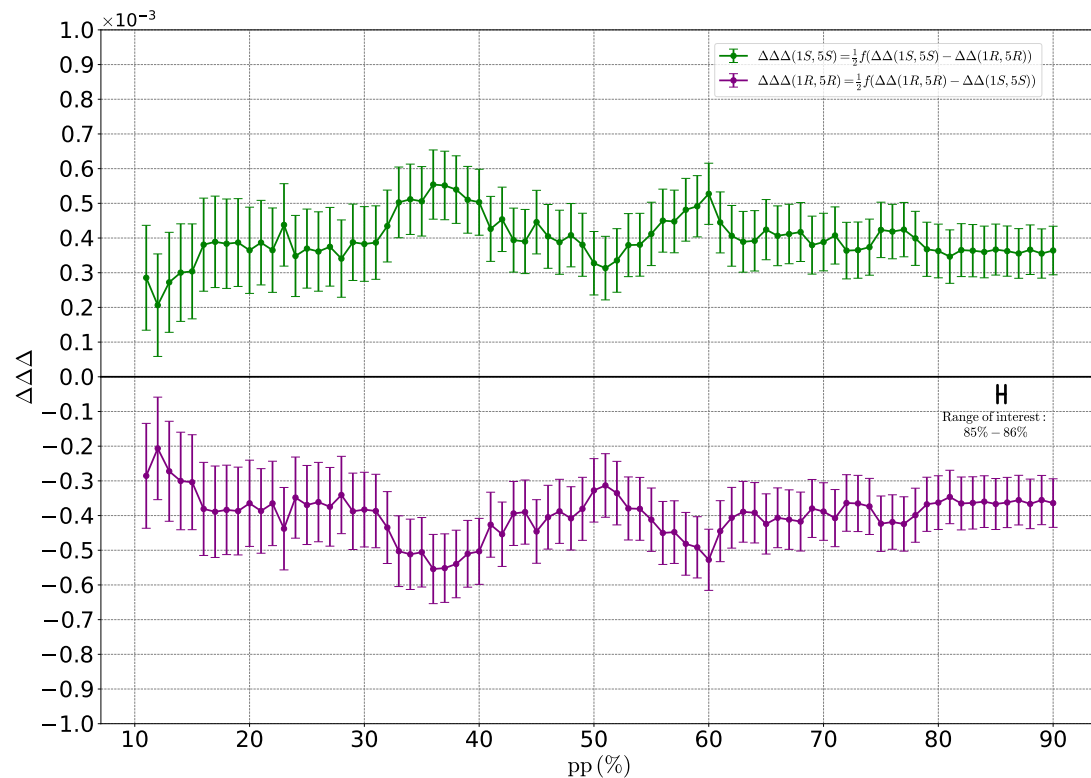


Figure 5.11: ‘Triple deltas’ $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ versus mask pixel percentage for a pair of measurement runs on the enantiomers of α -pinene.

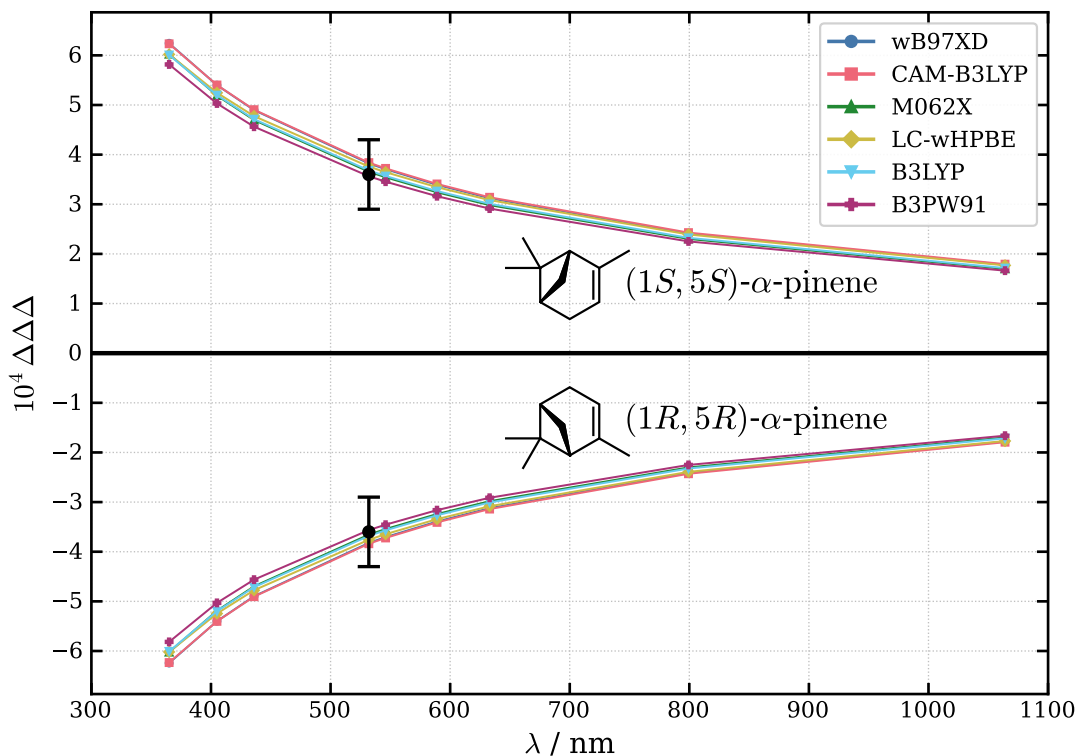


Figure 5.12: Measured ‘triple delta’ values $\Delta\Delta\Delta(1S, 5S)$ and $\Delta\Delta\Delta(1R, 5R)$ for the enantiomers of α -pinene (see black data points at $\lambda = 532$ nm). Also, quantum chemistry predictions for six different density functionals at the aug-cc-pVTZ basis set as a function of wavelength are plotted. The geometry optimisation was the same for all density functionals (B3LYP/6-311G++(d,p)) and was obtained from Autschbach’s OR45 benchmark [123].

The results quoted in our publication [121] of $\Delta\Delta\Delta(1S, 5S) = (+3.6 \pm 0.3) \times 10^{-4}$ and $\Delta\Delta\Delta(1R, 5R) = (-3.6 \pm 0.3) \times 10^{-4}$ were calculated using a slightly different but equally valid data analysis procedure developed independently by Dr. Aidan Arnold and applied to a larger pool of data deriving from multiple pairs of measurement runs, giving results matching (5.13) and (5.14) but with smaller uncertainties.

5.3 Viruses

Though it does not strictly qualify as “Rayleigh” optical activity due to the relatively large size of the scatterers, we also used our instrument to measure circular intensity differential scattering from viruses in solution. The promising first results described below suggest that our instrument, or a future variant of it, could prove useful for virus

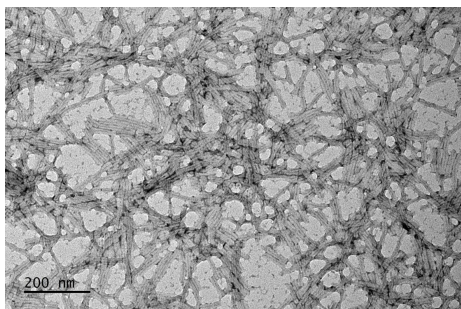
detection and characterisation.

5.3.1 Tobacco mosaic virus (TMV)

The first virus that we examined was tobacco mosaic virus (TMV), samples of which were provided by Prof. Andrew Love from the James Hutton Institute. TMV is a right-handed, single-stranded RNA virus of the genus *Tobamovirus*. It was the first virus to be discovered and its study is considered to have established the first principles of modern day virology [130, 131].

TEM analysis of isolated Tobacco mosaic virus (TMV) derived structures

Tobacco mosaic virus particles (agglomerations of high concentrations of 18x300nm rods)



Empty Tobacco mosaic virus particles (18nm rods of varying lengths- up to several microns long)

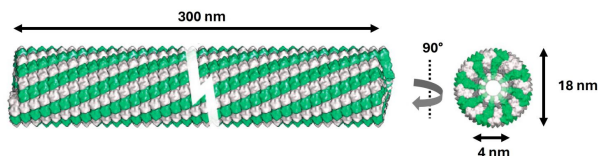
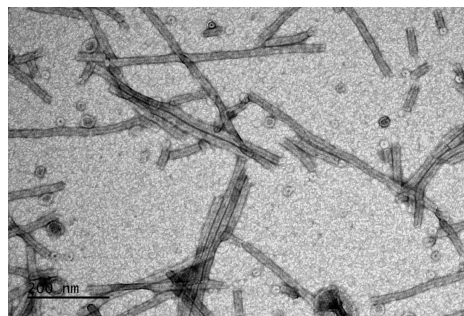


Figure 5.13: TEM analysis of isolated TMV derived structures. Images courtesy of Prof. Andrew Love from the James Hutton Institute.

As we can see in Fig. 5.13, TMV has a rod-like helical structure with length 300 nm, external diameter 18 nm and internal diameter 4 nm. This relatively large chiral geometry led us to hypothesise that TMV should exhibit relatively strong circular intensity differential scattering.

Shown in Fig. 5.14 is the ‘double delta’ $\Delta\Delta$ as a function of pixel percentage for a run on a 250 $\mu\text{g}/\text{mL}$ concentration of TMV in a sodium azide buffer solution. The sodium azide protects the virus from bacterial overgrowth. The underlying diagnostics are shown in Fig. 5.15, following the procedures previously described for α -pinene.

The value of the ‘double delta’ in the 85-86% pixel percentage range is $\Delta\Delta = (-5.15 \pm 0.01) \times 10^{-2}$, a significantly larger value when compared with our α -pinene results, as expected.

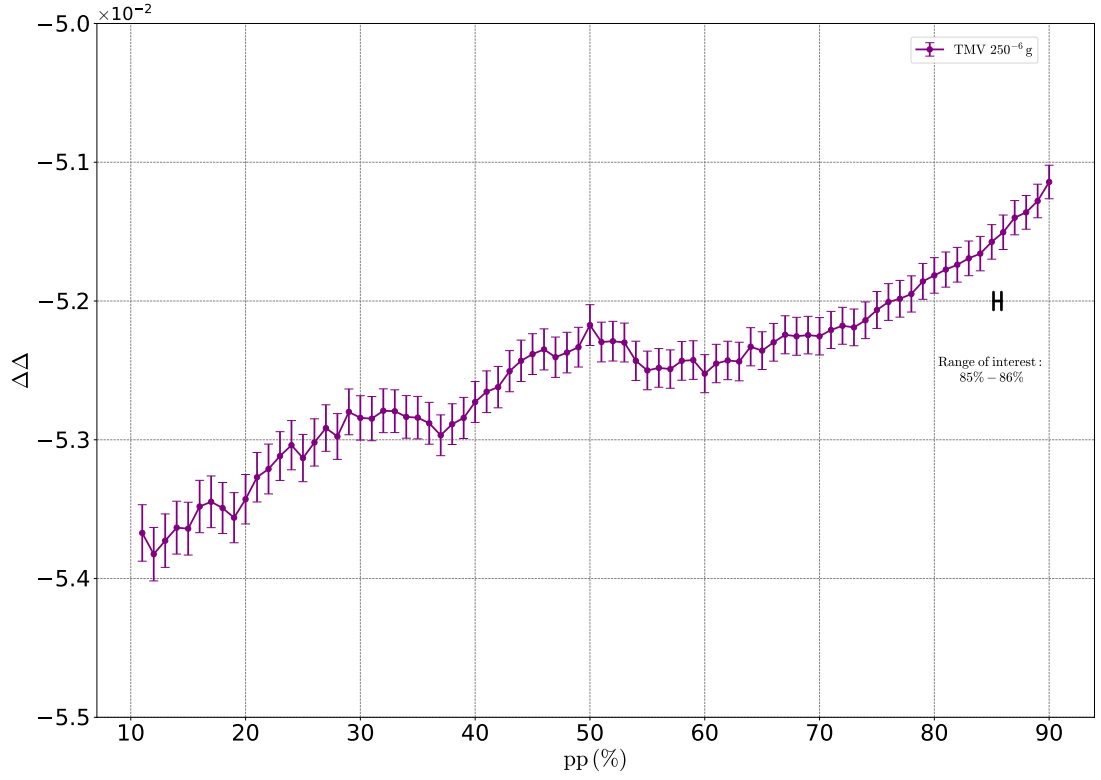


Figure 5.14: ‘Double delta’ $\Delta\Delta$ vs pixel percentage for a measurement run on TMV.

Chapter 5. Measurements of RayOA

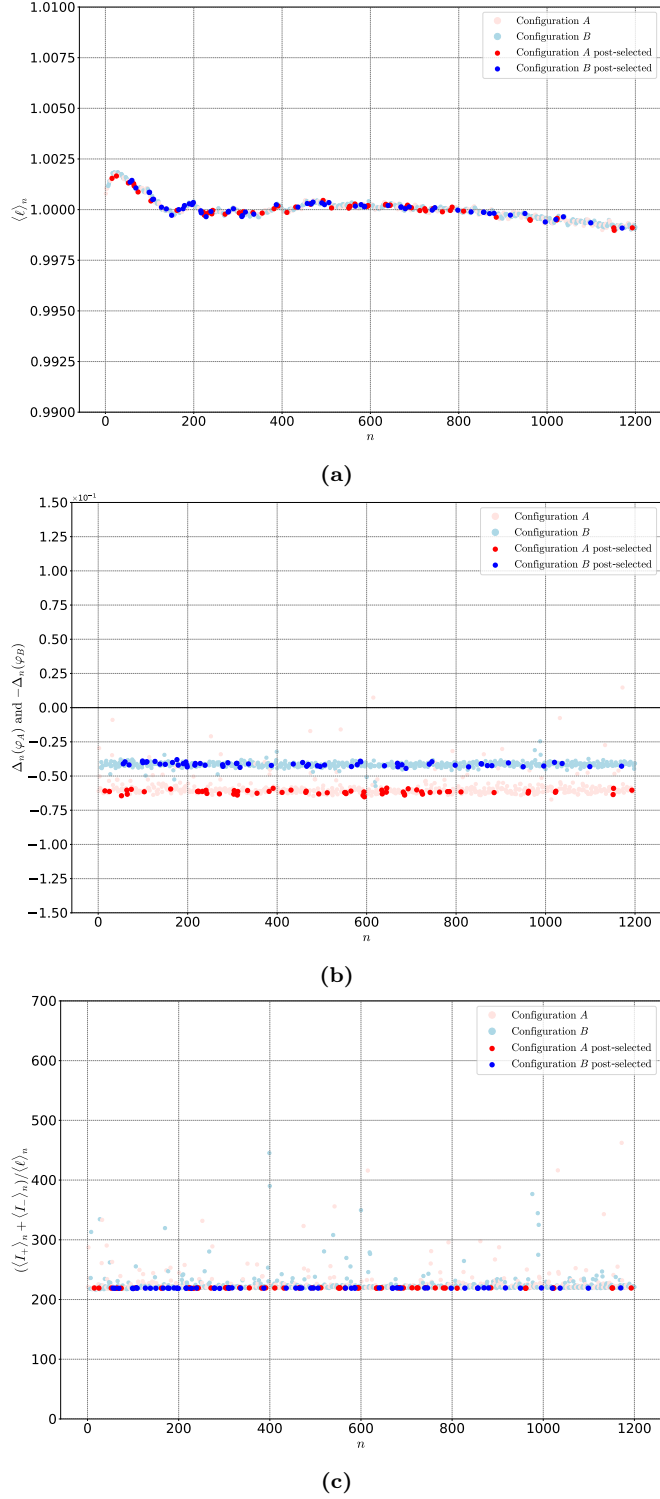


Figure 5.15: Diagnostics for a measurement run on TMV. (a): Normalised laser power $\langle \ell \rangle_n$ versus exposure number n . (b): ‘Single deltas’ $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus n . (c): Total measured signal $(\langle I_+ \rangle_n + \langle I_- \rangle_n)/\langle \ell \rangle_n$ versus n , normalised by $\langle \ell \rangle_n$ to correct for laser fluctuations.

5.3.2 Turnip yellow mosaic virus (TYMV)

The second virus that we examined was turnip yellow mosaic virus (TYMV), samples of which were also provided by Prof. Andrew Love. TYMV is a single-stranded RNA virus of the genus *Tymovirus*, with an icosahedral-shaped capsid. Unlike TMV, the overall structure of TYMV is achiral (icosahedral $T = 3$ symmetry) but it is composed of chiral substituents so it served as an interesting sample for our purposes. In Fig. 5.16, we can see the structure of TYMV. Its icosahedron-shaped capsid has a 28 nm diameter. Our initial hypothesis was that TYMV should produce only weak circular intensity differential scattering given the approximately spherical shape of the virus.

TEM analysis of isolated Turnip yellow mosaic virus (TYMV) derived structures

TYMV exists as 28 nm icosahedra with a $T=3$ symmetry

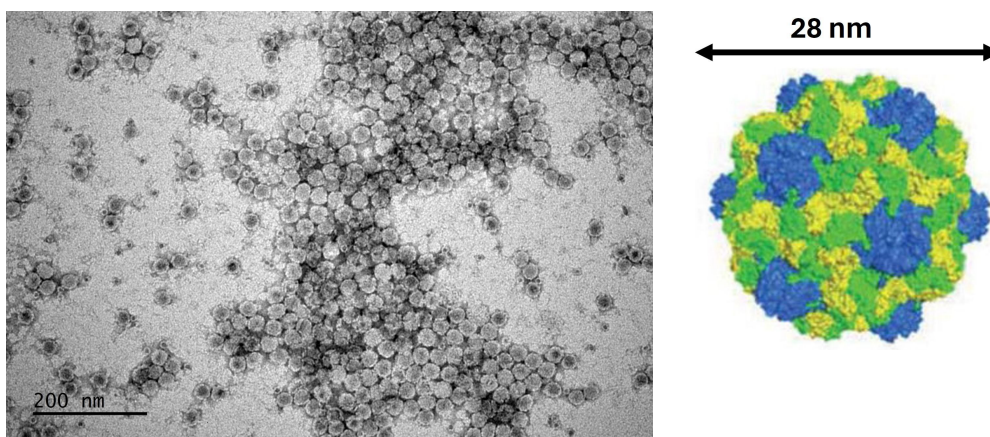


Figure 5.16: TEM analysis of isolated TYMV derived structures. Images courtesy of Prof. Andrew Love from the James Hutton Institute.

Shown in Fig. 5.17 is the ‘double delta’ $\Delta\Delta$ as a function of pixel percentage for a measurement run on a 300 $\mu\text{g}/\text{mL}$ concentration of TYMV, again in a sodium azide buffer solution to protect the virus from bacterial overgrowth. The underlying diagnostics are shown in Fig. 5.18, again following the procedures previously described for α -pinene.

The value of the ‘double delta’ in the 85-86% pixel percentage range is $\Delta\Delta =$

$(-4.46 \pm 0.02) \times 10^{-2}$, a value of the same order of magnitude as for TMV. This was surprising to us. While TYMV is comprised of protein subunits made from chiral amino acids, its overall shape is icosahedral with $T = 3$ symmetry and therefore possesses a quasi-spherical symmetry. This seems to suggest that the circular intensity differential scattering is more “sensitive” than we originally thought to chiral subunits within larger, otherwise non-chiral structures. Some interesting ideas and thought on this topic for further research are presented, among other things, in chapter 6.

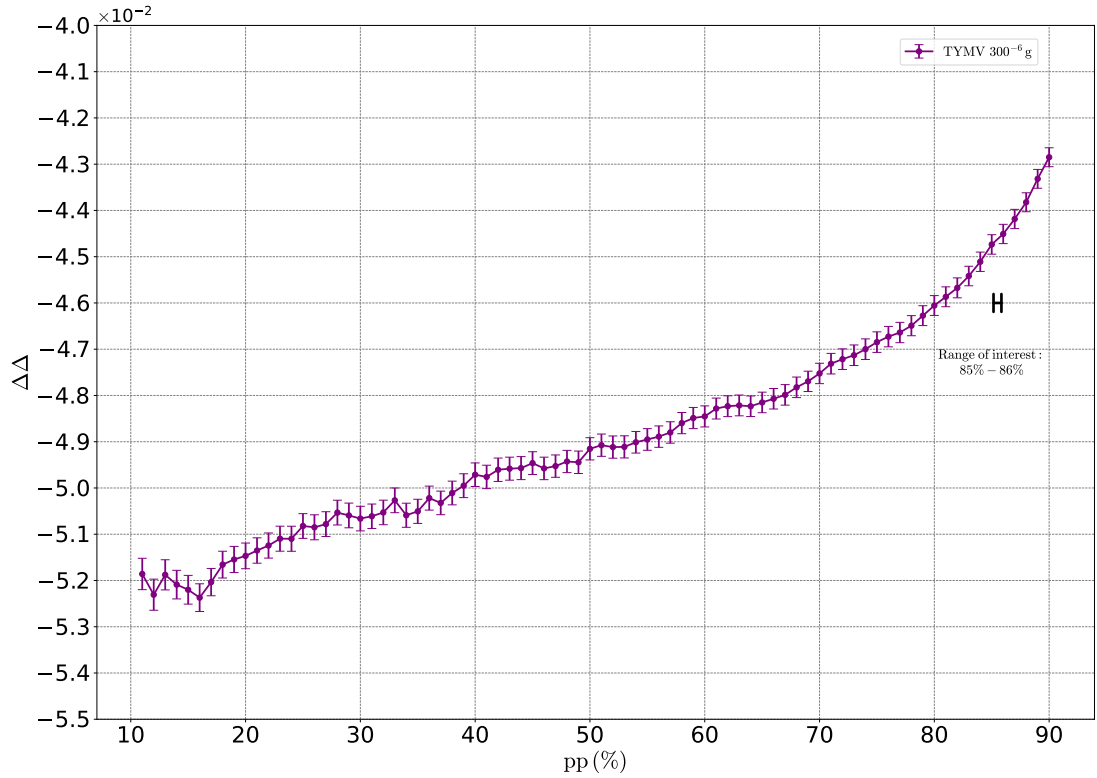


Figure 5.17: ‘Double delta’ $\Delta\Delta$ versus pixel percentage for a measurement run on TYMV.

5.4 Summary of Experimental Work

In this chapter, the complete experimental workflow for the data acquisition, analysis and measurement of RayOA was presented. From background acquisition and data collection, to noise reduction techniques and data preparation (image cropping, threshold filtering), the entire process was explained step-by-step, including a useful flow chart

Chapter 5. Measurements of RayOA

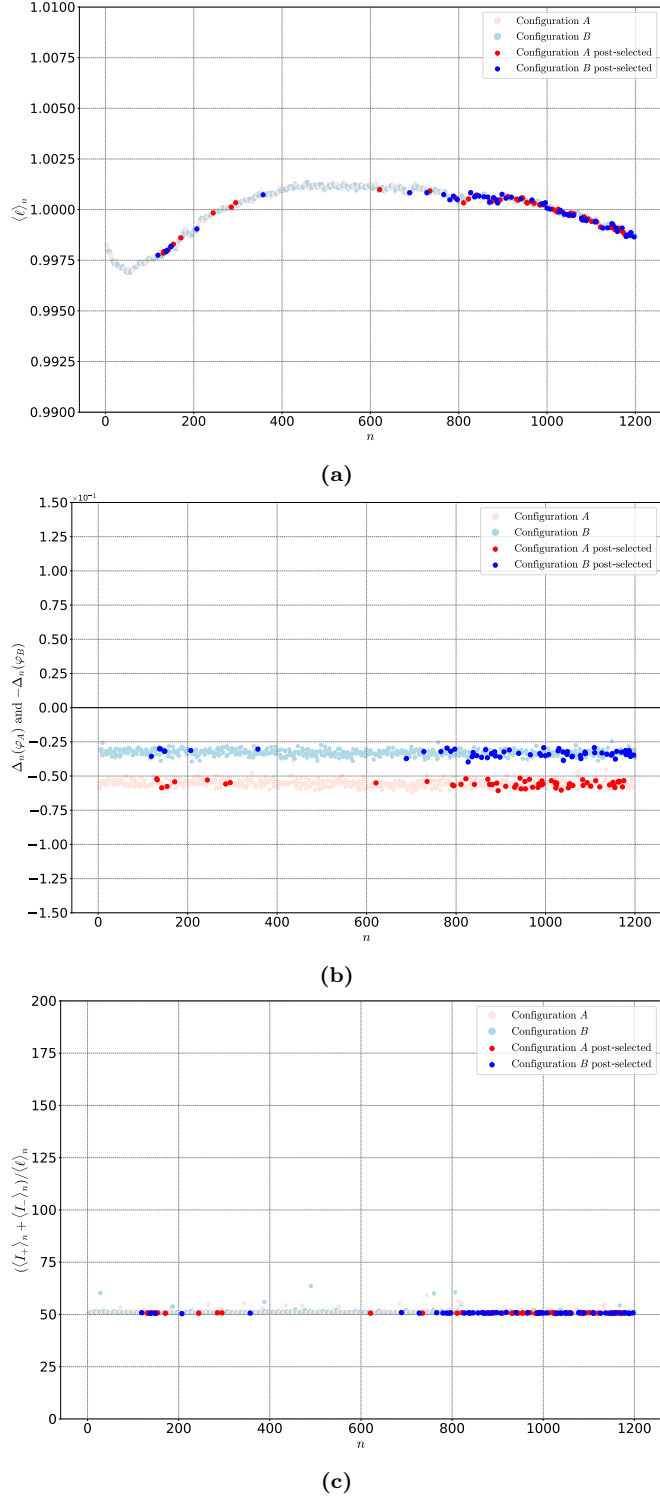


Figure 5.18: Diagnostics for a measurement run on TYMV. (a): Normalised laser power $\langle \ell \rangle_n$ versus exposure number n . (b): ‘Single deltas’ $\Delta_n(\varphi_A)$ and $-\Delta_n(\varphi_B)$ versus n . (c): Total measured signal $(\langle I_+ \rangle_n + \langle I_- \rangle_n) / \langle \ell \rangle_n$ versus n , normalised by $\langle \ell \rangle_n$ to correct for laser fluctuations.

that outlines all the steps sequentially.

Using this framework, RayOA circular intensity differentials were obtained for both enantiomers of α -pinene and were found to be $(+3.6 \pm 0.7) \times 10^{-4}$ for the $(1S, 5S)$ enantiomer and $(-3.6 \pm 0.7) \times 10^{-4}$ for the $(1R, 5R)$ enantiomer, in excellent agreement with our quantum chemical predictions. The same methodology was also applied to viruses in sodium azide buffer solution, giving tentative circular intensity differentials of $(-5.15 \pm 0.01) \times 10^{-2}$ for TMV and $(-4.46 \pm 0.02) \times 10^{-2}$ for TYMV. Unfortunately we do not possess theoretical predictions for these values as it would require significant computational resources to calculate due to their sheer size and complexity.

These results taken together, demonstrate a full cycle of raw data to useful RayOA final measurements. It remains for us to expand this framework into other samples to further establish this new chiroptical technique.

Chapter 6

Summary and Outlook

The work presented in this thesis is a comprehensive treatise on RayOA on a theoretical, computational and experimental basis. An extended theory was presented that expands the description of chiral light-matter interactions to include dense, neat-liquid molecular samples. In-depth quantum-chemical computational calculations were presented on the various polarisability tensors of α -pinene that served as a basis to compute a theoretical prediction on the magnitude and sign of its circular intensity differential Δ . Lastly, the design of a bespoke RayOA-dedicated optical instrument was presented along with the first experimental results of RayOA from α -pinene that were in precise agreement with the computational predictions. Additionally, provisional RayOA experimental results were presented for two viral samples, i.e. TMV and TYMV.

Our hope is that this bespoke instrument can be used by chemistry and biochemistry labs to robustly assign the absolute configuration of chiral molecules, measure the enantiomeric excess of chiral molecules in solution and other potentially more ‘exotic’ applications. To that end, we are currently attempting to patent the design as intellectual property (IP) and we already have commercial interest for its licensing by a private company.

Possible directions for future research are outlined below.

- The first-generation RayOA instrument described in this thesis is designed to operate at a single wavelength of 532 nm, ensuring that in theory our samples display

negligible absorption [132]. In practice however, we did observe a small amount of absorption from the α -pinene samples that was visible in the captured images, potentially due to residual impurities in the sample. It remains to perform measurements of RayOA at different wavelengths, with new information potentially available near or on resonance.

- In this work, we utilised the SCP configuration at a 90° scattering angle. Other implementations can be performed with different configurations (ICP [2], DCP [48]) and scattering angles that might potentially yield additional useful information.
- In this work, we present results for α -pinene which comes in neat liquid form and two viral samples in solution. It remains for us to perform measurements on small chiral molecules in dilute solution.
- In our experiment, the incident light was a single horizontally polarised beam. Future iterations of a similar experiment could attempt to illuminate samples with structured light, e.g. polarised standing waves [68] and vortex beams [70, 133].
- No static external magnetic or electric fields were applied to our samples. A potential extension to our work could include the addition of such fields in an attempt to measure electric or magnetic RayOA [116, 117].
- The neat α -pinene and virus solution samples used in this project were isotropic. Future measurements can be attempted on anisotropic samples like liquid crystals or thin films.
- We focused on anisotropic RayOA (rotational Raman optical activity), however potential extensions to isotropic RayOA, including the potential detection of chiral (acoustic) phonons scattered via RayBOA (e.g. α -quartz) [134], would be of interest.
- The neat α -pinene and virus solution samples used in this work are dense. Trying to detect a RayOA signal from a dilute (gaseous) chiral sample instead would be

an interesting variation to test the accuracy of quantum chemistry predictions based on single-molecule theory.

- Our current setup was housed on a breadboard of dimensions 45×60 cm. We are currently exploring options to miniaturise the experimental setup to aid in the aforementioned commercialisation efforts.
- The data presented here involved capturing approximately $N_A + N_B = 1200$ exposures each with a $\Delta t = 30$ s exposure time, giving a total measurement-run time of ~ 11 h per sample. It should be possible to significantly reduce this measurement time by increasing the incident laser power and/or the amount of scattered light collected. Rapid RayOA measurements could open the door to a wealth of potential applications such as real-time monitoring of chirality.

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