A Method to Measure the Circular Dichroism of Metal-Halide Perovskite Thin-Films

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ABSTRACT

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Chiral metal-halide perovskites have promise for application in spin-LEDs, circularly polarized light detectors, and electron spin filtering. In characterizing the chiroptical properties of a material, circular dichroism spectroscopy is critical. Circular dichroism (CD) is defined as the difference in absorption of left and right circularly polarized light. The CD spectra of thin films can have artifacts from anisotropies in the material which must be accounted for in the analysis of the data after making multiple measurements. Additionally, optical elements can introduce artifacts in the CD spectra. We have made a setup for measuring the circular dichroism of these perovskite thin films and a method for removing anisotropic artifacts from our data.

Keywords: circular dichroism spectroscopy, hybrid organic-inorganic perovskites, spectroscopic methods, polarization modulation

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Contents

List of Figures

Chapter 1

Introduction

Engineering the optoelectronic properties of metal-halide perovskites (MHPs) is an active area of research. MHPs are semiconductors that have shown a high degree of optical tunability by substituting the atoms and molecules in their structure. The high tunability of their optical properties makes MHPs suitable for use in light-emitting diodes (LEDs), solar cells, and photodetectors [1]. MHPs can be spin coated onto their substrates as thin films, making device production simple and inexpensive [1].

More recently, chiral perovskites are showing promise in the production and detection of circularly polarized light and electron spin filtering (only conducting electrons with certain spin) [2]. Circular dichroism (CD) is a key property of chiral materials/molecules in the UV-visible range [3]. Therefore, measuring the CD of chiral perovskites is essential to making progress in device development.

Measuring the CD of these thin films is more complicated than measuring the CD of molecules in solution. Anisotropies in the films leads to artifacts in the CD spectra that need to be compensated for [3–6]. Residual linear birefringence (LB) and linear dichroism (LD) in the measurement system also leads to artifacts in the CD signal which need to be corrected. We have found a method to correct for these artifacts and designed an optical bench setup to measure the CD of perovskite thin films.

1.1 Background

1.1.1 Circular Dichroism

The polarization of a light wave is the direction of oscillation of the electric field. Any polarization direction can be expressed as the sum of a vertically polarized component and a horizontally polarized component. When the oscillations of these components are out of phase by $\pi/2$ (90 degrees), the result is circularly polarized light as illustrated in Fig. 1.1.

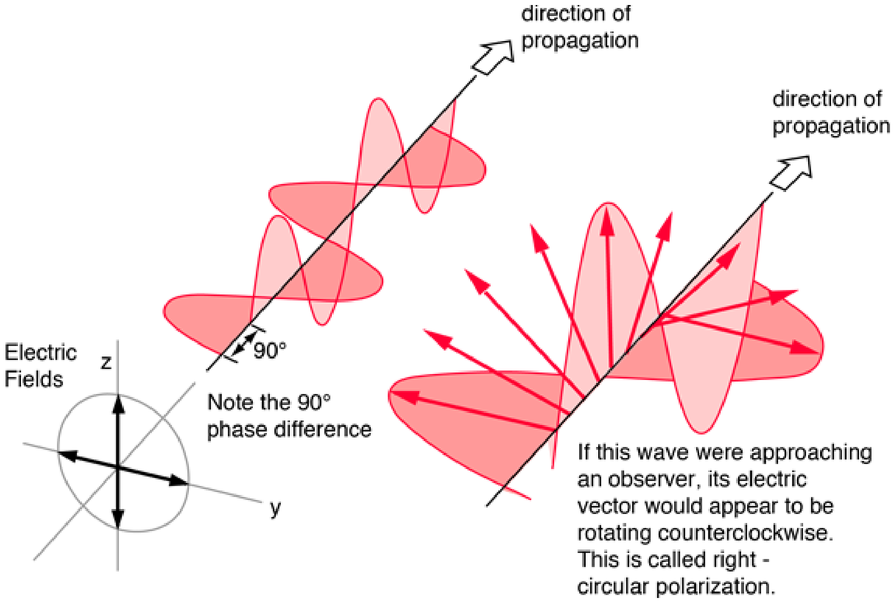

Figure 1.1 A depiction of circularly polarized light. On the left, a superposition of vertical and horizontal polarization components 90 degrees out of phase is shown. On the right, it is depicted how this causes the polarization vector to rotate as the light propagates. (From Ref. [7].)

The polarization vector is seen to rotate either clockwise (right circularly polarized, RCP) or counterclockwise (left circularly polarized, LCP) when looking at the source [8].

Circular dichroism is the property of a material to absorb left and right circularly polarized light differently. It is defined as the difference in absorption between left and right circularly polarized light

$$CD = \Delta A = A_L - A_R \tag{1.1}$$

where A_L and A_R are the absorbance of left and right circularly polarized light. Equation 1.1 is in absorbance units (AU) which are the easiest units to use in derivations involving CD. However, for historical reasons CD is usually reported in terms of ellipticity, which has units of millidegrees. To derive the conversion factor between AU and millidegrees, we start with the definition of the ellipticity of polarization,

$$\tan(\theta) = \frac{E_R - E_L}{E_R + E_L} \tag{1.2}$$

where E_R and E_L are the left and right circular polarization components of the electric field. The CD is small, which means θ is small and we can write $\tan(\theta) \approx \theta$. Since the intensity of light is proportional to the square of the electric field we can rewrite this in terms of the intensity of left and right circular polarization components (I_R and I_L),

$$\theta(\text{radians}) = \frac{I_R^{1/2} - I_L^{1/2}}{I_R^{1/2} + I_L^{1/2}}. \tag{1.3}$$

Now, we substitute Beer's law ($I = I_0 e^{-A\ln(10)}$) for the intensities and rearrange,

$$\theta(\text{radians}) = \frac{e^{-A_R\ln(10)/2} - e^{-A_L\ln(10)/2}}{e^{-A_R\ln(10)/2} + e^{-A_L\ln(10)/2}}, \tag{1.4}$$

$$= \frac{e^{\Delta A\ln(10)/2} - 1}{e^{\Delta A\ln(10)/2} + 1}. \tag{1.5}$$

Again using the fact that ΔA is small, we expand the exponentials to first order and discard the term with ΔA in the denominator since $\Delta A << 2$,

$$\theta(\text{radians}) = \frac{\Delta A \frac{\ln(10)}{2}}{\Delta A \frac{\ln(10)}{2} + 2}, \tag{1.6}$$

$$= \Delta A \left(\frac{\ln(10)}{4} \right). \tag{1.7}$$

We then convert from radians to millidegrees to get the final expression for CD in millidegrees,

$$\theta(\text{mdeg}) = \Delta A \left(\frac{\ln(10)}{4} \right) \left(\frac{180}{\pi} \right) (1000) \approx \Delta A(32982). \tag{1.8}$$

The path length through the material will affect the magnitude of CD, so sometimes the dissymmetry factor (usually denoted g, and sometimes g_{CD} or g_{abs}) is reported. This is just the CD (in AU) divided by the absorption (A), which corrects for differences in sample thickness, density, etc.

$$g = \frac{A_L - A_R}{A} \tag{1.9}$$

A material or molecule will exhibit circular dichroism if it is chiral. Chirality is just Greek for "handedness" and something is chiral if it shares the same asymmetry as your hand–meaning it isn't superimposable on its mirror image. Something can be either right (R) or left (S) chiral, and most chiral molecules have an R- and and S- form, called enantiomers.

The different absorption of LCP and RCP light is caused by selection rules in the material. Photons are bosons and so have integer spin; LCP photons have spin $+1$ (denoted σ^+) and RCP photons have spin -1 (denoted σ^-). The conservation of photon and electron angular momentum leads to the selection rules. For example, if a σ^+ photon excites a spin $-1/2$ electron then the electron must move into a spin $1/2$ state to conserve spin. If there are only spin $-1/2$ states available in the conduction band, then the photon will not be absorbed.

So, if at a certain energy there are more allowed transitions with a change of $+1$ spin, then more LCP photons will be absorbed. Looking at (1.1), there will be a positive CD signal in this case. If

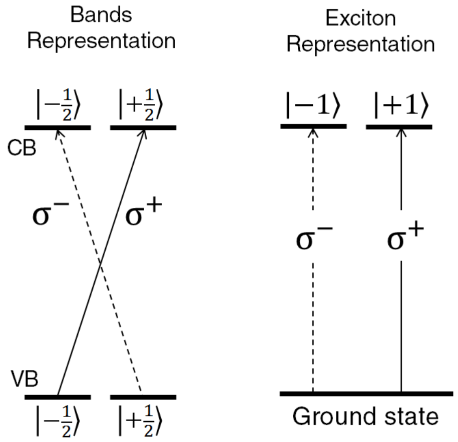

Figure 1.2 Two simplified representations of the selection rules for circularly polarized photon absorption. σ^+ and σ^- denote left and right circularly polarized photons with spin angular momentum $+1$ and -1 respectively. An electron in the valence band (VB) can only absorb a photon if there is an appropriate state in the conduction band (CB) that conserves angular momentum. The exciton representation shows that ground state excitons (spin 0) are excited to a ± 1 state, the availability of these states determines the absorption. (From Ref. [9].)

there are more -1 spin transitions then more RCP photons will be absorbed and there will be a negative CD signal. It is notable that left-handed chiral materials *do not necessarily* absorb more LCP light nor do right-handed materials necessarily absorb more RCP light.

1.1.2 Metal-Halide Perovskites

Metal-halide perovskites have the perovskite crystal structure ABX_3 as depicted in figure 1.3a. The metal cation (B), is surrounded by the halide anions (X_3). The specific materials we are interested in studying are 2D hybrid organic-inorganic metal-halide perovskites. This means that the A-site cation is a large organic molecule which splits up the structure into alternating layers of the metal-halide octahedra and organic molecules as in Fig. 1.3b.

The tunable optical properties of these materials comes from the ability to swap out the metal, halide, and organic molecule used. Typically the metal is tin or lead and the halide is iodine or

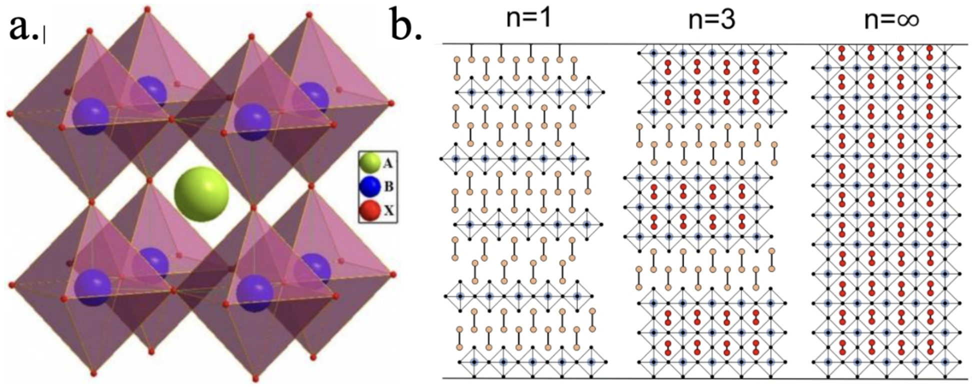

Figure 1.3 Perovskite crystal structure. Metal-halide perovskites have the perovskite crystal structure ABX_3 as depicted in (a). We are looking at 2D hybrid organic-inorganic metal-halide perovskites. This means that the B sites are occupied by metal atoms, the X sites are halide atoms (X_3) and the A site is a large organic molecule which splits up the structure into alternating layers of the metal-halide octahedra and organic molecules as in (b). (From Ref. [10].)

bromine. There are many other possible metals and halides that are used and research is constantly being done on finding more that work [11].

These perovskites can be chiral when the organic molecules are, or when the organic molecule distorts the crystal layer [2]. A specific chiral perovskite we plan to study is both the R- and S-forms of naphthylethylammonium lead bromide (R- or S-NPB). This perovskite is chiral because the organic molecule (naphthylethylammonium) in it is chiral. Its structure is shown in Fig. 1.4.

R-, S-, and racemic NPB have been studied before by Jana et al. [12], and so provide a good benchmark for our new system for measuring CD of other perovskite thin films.

1.2 Past Work

Aside from Jana et al, other researchers have measured the CD of various perovskite thin films and their other properties. Coccia et al. [13] studied chiral lead-free perovskites and compared them to their leaded counterparts (such as comparing two identical perovskites aside from bismuth

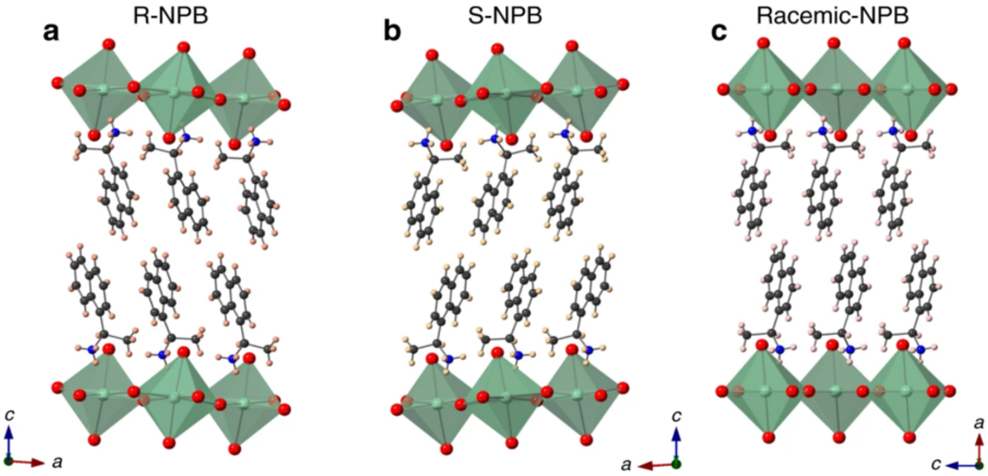

Figure 1.4 The structure of R-, S-, and racemic naphthylethylammonium lead bromide (NPB), a chiral perovskite we took the CD spectrum of. (a) shows the right handed form, (b) shows the left handed form, and (c) shows the racemic form. The chiral organic molecule, naphthylethylammonium, distorts the octahedral layers and gives the whole perovskite the same chirality as itself. The racemic form incorporates equal amounts of R- and S-naphthylethylammonium, giving it zero net chirality. (From Ref. [12].)

substituted for lead in one of them). We have future plans to measure some of the same perovskites as Coccia et al. at room temperature and low temperature.

The physical setup to measure CD detailed in the next section is well known, but an analysis of how the system works is important to understand how to correct for anisotropies in the sample. The analysis of our system detailed in Section 2.2 is not new, and relies on the information published by Drake [14], Ugras et al. [5], and Sutherland [15]. In the next chapter, I will go into detail about how their work supports ours.

Chapter 2

Methods

2.1 Experimental Setup

As stated in the introduction, circular dichroism (CD) is the difference between the absorption of left and right circularly polarized light. This difference in absorption can either be measured directly with two beams, or by modulating the polarization of one beam and using a lock-in amplifier.

The two beam technique involves sending one LCP and one RCP beam through the sample at the same spot and measuring the differential absorption directly. This is difficult because the two beams need to be well aligned and their relative intensities before and after the sample need to be known. This could be accomplished by splitting one beam and knowing the reflectance/transmission of the beam splitter extremely well, but the inclusion of the beam splitter makes this method impractical for us. We decided to use a one beam technique since this is the most common method used and involves much less alignment. The one beam setup is illustrated in Fig. 2.1.

In our setup, we use a xenon arc lamp as the light source. The light from the lamp is sent through a monochromator, a vertical wire grid polarizer, a photoelastic modulator (PEM) at 45 degrees and set to quarter wave retardance, the sample, and finally into a photodiode. To measure

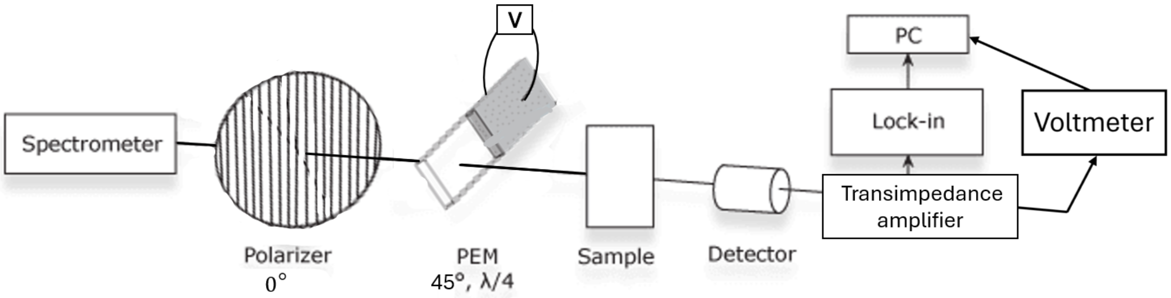

Figure 2.1 Typical setup for circular dichroism. The light from a xenon arc lamp (not depicted) is sent through a spectrometer, a vertical wire grid polarizer, a photoelastic modulator (PEM) at 45 degrees, the sample, and finally into a photodiode. The signal from the photodiode is sent through a transimpedance amplifier then to a voltmeter and a lock-in detector referencing the PEM frequency. The data from the lock-in and voltmeter is sent to a computer for processing. The PEM is set to quarter wave retardance. (From Ref. [16]).

temperature-dependent CD, the sample is also placed inside a cryostat which has windows before and after the sample. The signal from the photodiode is sent through a transimpedance amplifier then to a voltmeter and a lock-in detector referencing the PEM frequency.

To understand what is being measured, notice that since the PEM is set to quarter wave retardance and oriented 45 degrees from the polarizer, the light exiting the PEM will alternate sinusoidally between left (LCP) and right (RCP) circularly polarized light. The lock-in amplifier is measuring the amplitude of this oscillation after it passes through the sample. I will refer to this as the AC signal, or I_{AC}. The voltmeter measures the DC offset of the signal from the photodiode, which is the average intensity of the light passing through the sample. I will call this the DC signal, or I_{DC}.

It is unintuitive how this measurement gives CD as defined in (1.1). The AC signal is essentially the difference between the intensity of LCP and RCP light at the detector, but not quite. The next section covers how we go from the measured AC and DC intensities to the circular dichroism.

2.2 Analysis of Experimental Setup

To start with the end in mind, CD is related to the AC and DC signals by the following equation.

$$CD(\text{mdeg}) = \frac{32982}{\ln(10) J_1(\delta_0)} \frac{I_{AC}}{I_{DC}} \tag{2.1}$$

The goal of this section is to understand where each factor in this equation comes from. Understanding this equation makes it easier to troubleshoot the CD setup we use and analyze results.

A similar analysis to the following can be found in the works of Drake [14], Urgas et al. [5], and Sutherland [15]. This derivation most closely follows Sutherland; the others use Mueller matrices in their derivation. The two methods give the same result, but Mueller matrices require more background knowledge than was reasonable to include here. For this same derivation using Mueller matrices, see Appendix A.

First, the retardance induced by the PEM (δ) is given by (2.2) where $\delta_0 = \pi/2$ is the peak retardance and ω is the oscillation frequency.

$$\delta(t) = \delta_0 \sin(\omega t) \tag{2.2}$$

The light emerging from the PEM can be described as a sum of left and right circularly polarized components (2.3). The PEM causes the light to switch between these two components as in (2.4) and (2.5).

$$I_0(t) = I_R(t) + I_L(t) \tag{2.3}$$

$$I_L(t) = \frac{I_0}{2}[1 + \sin\delta(t)] \tag{2.4}$$

$$I_R(t) = \frac{I_0}{2}[1 - \sin\delta(t)] \tag{2.5}$$

In these equations I_R and I_L are the intensities of RCP and LCP light respectively, and I_0 is the total intensity of the beam.

Now, as the light travels through the sample I_R and I_L will change as the RCP and LCP light is absorbed. There will be a different absorption for each of these components denoted A_R and A_L

respectively. The intensity of the beam after the sample at the detector is given by,

$$I(t) = I_L(t)10^{-A_L} + I_R(t)10^{-A_R}. \tag{2.6}$$

Substituting (2.4) and (2.5) into (2.6) we find,

$$\begin{aligned} I(t) &= \frac{I_0}{2}(1+\sin\delta(t))10^{-A_L} + \frac{I_0}{2}(1-\sin\delta(t))10^{-A_R} \\ &= \frac{I_0}{2}(10^{-A_L} + 10^{-A_R} + \sin\delta(t)(10^{-A_L} - 10^{-A_R})). \end{aligned}$$

Since the CD is much smaller than the total absorption ($A_L - A_R << (A_L + A_R)/2$) we can expand the exponentials to first order as Taylor series. We find that $\frac{10^{-A_L}+10^{-A_R}}{2} \approx 10^{-\frac{A_L+A_R}{2}}$ and,

$$I(t) = I_0 10^{-\frac{A_L+A_R}{2}}(1 + \frac{1}{2}\sin\delta(t)\ln(10)(A_L - A_R)). \tag{2.7}$$

Finally the CD as defined in (1.1) shows up!

The lock-in amplifier will be measuring a sine wave at frequency ω: the modulation frequency of the PEM. So, we can expand the sine in terms of Bessel functions using (2.2) and discard all terms not at frequency ω.

$$\sin(\delta_0 \sin(\omega t)) = 2J_1(\delta_0)\sin(\omega t) + 2J_3(\delta_0)\sin(3\omega t)... \tag{2.8}$$

Plugging the first term into (2.7) and rewriting $A_L - A_R = CD$ and $\frac{A_L+A_R}{2} = A$ we find,

$$I(t) = I_0 10^{-A}(1 + J_1(\delta_0)\ln(10)CD\sin(\omega t)). \tag{2.9}$$

We can see that the signal is made of two terms, one modulated by a sine, $I_{AC} = I_0 10^{-A} J_1(\delta_0)\ln(10)CD$ and the other is just the transmitted intensity, $I_{DC} = I_0 10^{-A}$. These two terms are exactly what we are measuring with the lock-in amplifier and the voltmeter.

$$I(t) = I_{DC} + I_{AC}\sin(\omega t). \tag{2.10}$$

If we take the ratio I_{AC}/I_{DC},

$$\frac{I_{AC}}{I_{DC}} = J_1(\delta_0)\ln(10)CD,$$

$$CD = \frac{1}{\ln(10) J_1(\delta_0)} \frac{I_{AC}}{I_{DC}}. \tag{2.11}$$

Now we have an expression for CD in absorption units, (2.11). Using (1.8) we convert to millidegrees to get the final expression for CD in the units we want.

$$CD(\text{mdeg}) = \frac{32982}{\ln(10) J_1(\delta_0)} \frac{I_{AC}}{I_{DC}} \tag{2.12}$$

2.2.1 Dealing With Anisotropies

The analysis so far applies to measuring circular dichroism of molecules in solution. There is an additional consideration when measuring thin film samples, anisotropies. If the thin film has linear dichroism (LD) and linear birefringence (LB) then these will contribute to the measured CD despite not being related to the chirality of the sample. LD is defined as the difference between the absorption of vertical and horizontally polarized light. LB is the difference between the refraction of vertical and horizontally polarized light.

Since the PEM is varying the polarization sinusoidally, it is also varying the polarization between vertical and horizontal light, just 90 degrees out of phase with where the light is fully RCP or LCP. The light emerging from the PEM can also be thought of as a sum of vertical and horizontally polarized components. Considering this, (2.3) holds equally well for vertical/horizontal polarized light, except instead of the sine in (2.4) and (2.5) it is a cosine. To correctly analyze this requires the use of Mueller matrices, but in the end (2.10) gets an additional AC term, CD_{LDLB}.

$$I_{AC} = I_0 10^{-A} J_1(\delta_0) \ln(10) (CD + CD_{LDLB})) \tag{2.13}$$

The mathematical origin of the additional term can be seen in the derivation in Appendix A which is a somewhat simplified version of the derivation included in the works of Ugras et al. [5] and Yao, et al. [17].

Since we want to learn about the chirality of the sample, we need to get rid of this last term since it is unrelated to the chirality. The physical origin of the C_{LDLB} term comes from a misalignment of the principal axes of the *LD* and *LB* [17]. This term changes sign depending on which direction the light is traveling through the sample since the angle between the principle axes of the *LD* and *LB* changes sign after flipping the sample [4, 5, 17]. So by taking a measurement with the light entering the front and another entering the back and then averaging them, this last term vanishes.

Other elements in the system aside from the sample can have residual birefringence which also contribute to the measured CD. To correct for these, it is standard practice to measure the CD of the system with no sample in place as a baseline, then subtract it off [18, 19].

In the next two chapters I present and discuss the tests I did to evaluate whether or not this method works in practice and suggest how the system could be improved.

Chapter 3

Results

To check if the system we set up worked, I took the CD spectrum of the system with no sample or cryostat windows as a baseline, another of the cryostat windows in place facing one way, and one more with the cryostat windows facing the other way. The cryostat windows we have are made of 5mm thick uncoated fused silica. They are not chiral, so should have no chiral contribution to the CD. They do exhibit some LD and LB, which will cause them to exhibit some CD. The results are plotted in Fig. 3.1a along with the average of the two CD spectra of the cryostat windows.

The CD of the system with no sample in it (the baseline) is nonzero and shows wavelength dependence. This is likely from residual birefringence in some part of the measurement system, such as the PEM. The CD spectra of our cryostat windows has the same shape as measuring no sample, except the signal is shifted up or down depending on the direction the windows are facing. The results of subtracting the baseline from the spectra of the windows and averaging the results are shown in Fig. 3.1b. Subtracting the CD of the system as a baseline gives a CD signal with minimal wavelength dependence on the order of 0.7 mdeg. Averaging the results of the subtraction gives a signal near zero mdeg, but not quite.

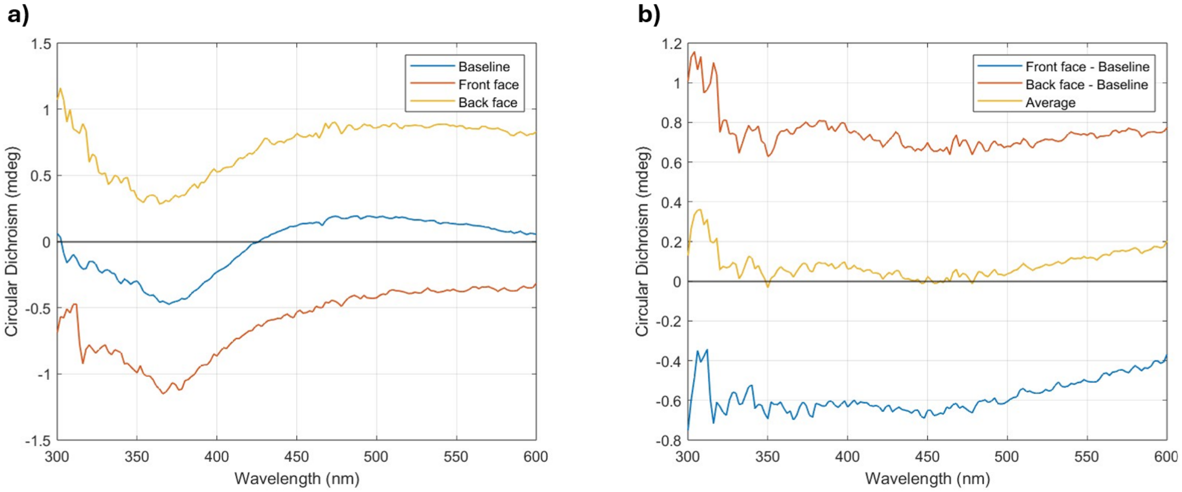

Figure 3.1 (a) Circular dichroism (CD) of the measurement system with no sample in it (baseline) and of the cryostat windows facing front and back. The system measures nonzero CD with no sample in place. When measuring the CD of our cryostat windows, the signal shape is the same except it is shifted up or down based on the direction the windows are facing when measured. The average of the CD spectra of the windows facing both ways is not zero. (b) The difference between the CD spectra facing each way and the baseline from (a) as well as the average of those two differences. Subtracting the CD of the system as a baseline gives a CD signal with minimal wavelength dependence on the order of 0.7 mdeg. Averaging the results of the subtraction gives a signal near zero mdeg, but not quite.

Chapter 4

Discussion

Initially the CD spectra of the cryostat windows was confusing since the CD of the windows should purely be a result of LD and LB (the windows are not chiral). So, the CD spectra of the windows facing one way versus the other should differ by a negative sign. As Fig. 3.1a shows, the spectra do not differ by a negative sign but are only shifted; if they did differ by a negative sign their peaks would face away from each other and their average would be zero.

Later, I measured the CD of the system with no sample in place to find that the shape of the CD spectrum was coming from some residual birefringence in the system itself. After subtracting this as a baseline it seems that the CD of the windows doesn't have strong wavelength dependence and the spectrum does flip sign when the windows are facing the opposite direction as seen in Fig. 3.1b.

Averaging the true CD spectra of the cryostat windows facing front and back gives the expected result of eliminating the CD. This shows that the we can remove the effects of the cryostat windows and the residual birefringence of the system using the method outlined in Chapter 2.

4.1 Conclusion

The component of the CD spectrum that is dependent on the chirality of a sample can be isolated by subtracting the baseline then averaging the CD spectra of the sample facing front and back. This also corrects for the residual CD in the system including the cryostat windows. This is exactly as predicted by the analysis done by Ugras, et al. and Sutherland [5, 15] and replicated here in Chapter 2 and Appendix A.

More rigorous checks need to be done by measuring the CD of actual samples and comparing the results to those in current literature such as Coccia, et al. and Jana, et al. [12, 13]. This would increase confidence in the instrumental correction factors and the method itself.

The signal to noise ratio (S/N) could also be improved by using a more intense light source. The S/N is sensitive to the intensity of the light at the detector. More light will increase the magnitude of the AC and DC signals and bring them out of the regime of electrical noise in the measurement equipment while leaving the actual magnitude of the CD unchanged. I believe noise is what causes the CD to not go to zero after averaging the CD spectra since the data collected was consistently noisier below 400 nm, a region where we know our light source and monochrometer are less efficient. The DC signal is also sensitive to ambient light, and ensuring that the only light at the detector is passing through the sample is critical to get an accurate CD spectrum. Building an enclosure for the measurement system would likely increase the S/N even further.

Appendix A

Mueller Matrix Analysis

Here I will repeat the derivation of the equation to calculate CD done in the section 2.2 except using Mueller matrices. The result is the same, although this is the rigorous way to do the analysis. In an effort to keep this brief, a knowledge of Stokes vectors and Mueller matrices is assumed. I will start by laying out all of the matrices involved in the calculation, then find the intensity at the detector, and finally interpret the intensity at the detector as the lock-in amplifier and voltmeter would. This is the version of the derivation that most closely follows Ugras [5, 17] and Drake [14].

First, the light before the PEM is horizontally polarized. The Stokes vector for horizontally polarized light is

$$S_{in} = [1, 1, 0, 0] \tag{A.1}$$

The light then passes through the PEM which has Mueller matrix,

$$M_{PEM} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\delta(t) & \sin\delta(t) \\ 0 & 0 & -\sin\delta(t) & \cos\delta(t) \end{pmatrix} \tag{A.2}$$

where $\delta(t) = \delta_0 \sin(\omega t)$ is the retardance from the PEM, ω is the modulation frequency of the PEM, and δ_0 is the peak retardance. The PEM is oriented at 45 degrees from the vertical, so the rotation Mueller matrix is also needed,

$$R(\theta) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\theta) & \sin(2\theta) & 0 \\ 0 & -\sin(2\theta) & \cos(2\theta) & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{A.3}$$

Next, the light passes through the sample. The Mueller matrix of the sample, M, does not directly contain information about its optical properties. The optical properties are directly seen in the differential Mueller matrix, m. The two are related by [5, 17],

$$M = 10^m. \tag{A.4}$$

The definition of m is [5, 17],

$$m = \begin{pmatrix} -A & -LD_{90} & -LD_{45} & CD \\ -LD_{90} & -A & CB & LB_{45} \\ -LB_{45} & -CB & -A & -LB_{90} \\ CD & -LB_{45} & LB_{90} & -A \end{pmatrix} \tag{A.5}$$

where A is the absorbance of the sample, LD and LB are the linear dichroism and birefringence, and CD and CB are the circular dichroism and birefringence. The subscripts on LD and LB denote the 0/90 degree and 45/135 degree components. Separating out the absorbance,

$$m = -A\mathbf{I} + \begin{pmatrix} 0 & -LD_{90} & -LD_{45} & CD \\ -LD_{90} & 0 & CB & LB_{45} \\ -LB_{45} & -CB & 0 & -LB_{90} \\ CD & -LB_{45} & LB_{90} & 0 \end{pmatrix} = -A\mathbf{I} + P. \tag{A.6}$$

Now,

$$M = 10^{-A\mathbf{I}}10^{P}. \tag{A.7}$$

Expanding 10^P to second order using (A.4) (second order is considered sufficient for moderately anisotropic samples [5]),

$$M = 10^{-A\mathbf{I}}\left(\mathbf{I} + \ln(10)P + \frac{1}{2}\ln(10)^2P^2\right). \tag{A.8}$$

Now, the Mueller matrix M is written in terms of the actual optical properties of the sample. Calculating the Stokes vector after the sample using these matrices gives,

$$\begin{aligned} S_{out} &= MR(-\pi/4)M_{PEM}R(\pi/4)S_{in} && \text{(A.9)} \\ &= M[1, \cos\delta(t), 0, \sin\delta(t)] && \text{(A.10)} \end{aligned}$$

The detector will only measure the first component of S_{out} (the intensity at the detector), (A.10) gives the first element of S_{out} as,

$$\begin{aligned} I_{detector} = 10^{-A}\Bigg[& 1 + \frac{1}{2}\ln(10)^2\left(CD^2 + LD^2 + {LD_{45}}^2\right) \\ & + \sin\delta(t)\left(\ln(10)CD + \frac{1}{2}\ln(10)^2\left(-LD \cdot LB_{45} + LD_{45} \cdot LB\right)\right) \\ & + \cos\delta(t)\left(-\ln(10)LD + \frac{1}{2}\ln(10)^2\left(-CD \cdot LB_{45} + CB \cdot LD_{45}\right)\right)\Bigg]. \end{aligned} \tag{A.11}$$

There is one DC term and two AC terms, one modulated by the sine and the other by cosine. The DC component, $I_{DC} = 10^{-A}\left(1 + \frac{1}{2}\ln(10)^2\left(CD^2 + LD^2 + {LD_{45}}^2\right)\right)$, is the mean transmittance of the sample and is a constant. Since CD, LD, and LD_{45} are small, the second term is negligible and $I_{DC} \approx 10^{-A}$. It is effectively the same as what we found for I_{DC} in Section 2.2.

The composition of trigonometric functions can be expanded as Bessel functions using (2.8) and

$$\cos(\delta_0 \sin(\omega t)) = J_0(\delta_0) + 2J_2(\delta_0)\cos(2\omega t) + 2J_4(\delta_0)\cos(4\omega t)... \tag{A.12}$$

Only the terms at frequency ω are kept by the lock-in amplifier. After expanding and only keeping the terms at ω,

$$\sin\delta(t) = 2J_1(\delta_0)\sin(\omega t), \tag{A.13}$$

$$\cos\delta(t) = 0. \tag{A.14}$$

Plugging these into (A.11),

$$I_{detector} = I_{DC} + (10^{-A})J_1(\delta_0)\sin(\omega t)\left[\ln(10)CD + \frac{1}{2}\ln(10)^2\left(-LD\cdot LB_{45} + LD_{45}\cdot LB\right)\right]. \tag{A.15}$$

The AC component has two parts: the actual CD and a contribution from the LD and LB which I will call CD_{LDLB}.

$$I_{AC} = (10^{-A})\ln(10)J_1(\delta_0)\left(CD + CD_{LDLB}\right) \tag{A.16}$$

As mentioned in Section 2.2, C_{LDLB} appears when the principal axes of the LD and LB are misaligned. When the sample is flipped front to back, the sign of the angle between the principal axes will change, which means the sign on CD_{LDLB} will also change [17]. So by averaging two scans, one with the sample facing each way, that term will vanish. After averaging, the ratio I_{AC}/I_{DC} is,

$$\frac{I_{AC}}{I_{DC}} = \ln(10)J_1(\delta_0)CD \tag{A.17}$$

So, our final expression for CD in absorption units is,

$$CD = \frac{1}{\ln(10)J_1(\delta_0)}\frac{I_{AC}}{I_{DC}} \tag{A.18}$$

which is the same as what we found in Section 2.2.

Bibliography

[1] O. Ostroverkhova, “Organic Optoelectronic Materials: Mechanisms and Applications,” Chemical Reviews **116,** 13279–13412 (2016).

[2] H. Lu, Z. V. Vardeny, and M. C. Beard, “Control of light, spin and charge with chiral metal halide semiconductors,” Nature Reviews Chemistry **6,** 470–485 (2022).

[3] G. Albano, G. Pescitelli, and L. D. Bari, “Chiroptical Properties in Thin Films of pi-Conjugated Systems,” Chemical Reviews **120,** 10145–10243 (2020).

[4] Y. Shindo, “Application of polarized modulation technique in polymer science,” Optical Engineering **34,** 3369 – 3384 (1995).

[5] T. J. Ugras, Y. Yao, and R. D. Robinson, “Can we still measure circular dichroism with circular dichroism spectrometers: The dangers of anisotropic artifacts,” Chirality **35,** 846–855 (2023).

[6] A. Abhervé, “Experimental Evidence of the Molecular and Macroscopic Origins of Circular Dichroism in Chiral Metal-Halide Networks,” Advanced Optical Materials 12 (2024).

[7] “Classification of polarization,” Hyperphysics (2025).

[8] “Circular polarization,” Wikipedia (2025).

[9] D. Giovanni, Ph.D. thesis, Nanyang Technological University, 2017.

[10] E. McClure, “Dielectric spectroscopy on 2D and 3D metal halide perovskites using an interdigitated electrode geometry,” (2022).

[11] K. R. Hansen *et al.*, “Mechanistic origins of excitonic properties in 2D perovskites: Implications for exciton engineering,” Matter **6,** 3463–3482 (2023).

[12] M. K. Jana, R. Song, H. Liu, D. R. Khanal, S. M. Janke, R. Zhao, C. Liu, Z. V. Vardeny, V. Blum, and D. B. Mitzi, “Organic-to-inorganic structural chirality transfer in a 2D hybrid perovskite and impact on Rashba-Dresselhaus spin-orbit coupling,” Nature Communications **11,** 4699 (2020).

[13] C. Coccia, M. Moroni, and L. Malavasi, “Chiral Metal Halide Perovskites: Focus on Lead-Free Materials and Structure-Property Correlations,” Molecules 28 (2023).

[14] A. F. Drake, “Polarisation modulation-the measurement of linear and circular dichroism,” J. Phys. E: Sci. Instrum 19 (1986).

[15] J. C. Sutherland, “Simultaneous measurement of circular dichroism and fluorescence polarization anisotropy,” In *Clinical Diagnostic Systems: Technologies and Instrumentation*, G. E. Cohn, ed.,**4625,** 126 – 136 (SPIE, 2002).

[16] “Circular dichroism,” Hinds Instruments (2024).

[17] Y. Yao, T. J. Ugras, T. Meyer, M. Dykes, D. Wang, A. Arbe, S. Bals, B. Kahr, and R. D. Robinson, “Extracting Pure Circular Dichroism from Hierarchically Structured CdS Magic Cluster Films,” ACS Nano **16,** 20457–20469 (2022).

[18] A. Rodger and D. Marshall, “Beginners guide to circular dichroism,” The Biochemist **43,** 58–64 (2021).

[19] N. J. Greenfield, “Using circular dichroism spectra to estimate protein secondary structure,” Nature Protocols **1,** 2876–2890 (2007).

Index