Electroabsorption as a Method to Accurately Measure the Exciton Binding Energy and Band Gap in 2D Metal Halide Perovskites

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ABSTRACT

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Electroabsorption is a technique used to extract further information from the absorption spectrum of a semiconducting material. Such materials have a band gap, the difference in energy from their valence and conduction bands, and they also often form excitons which have slightly less binding energy than the band gap. While the energy of the first excitonic state E_{1s} can readily be obtained from the typical absorption spectrum, the feature of band gap energy (E_g) and therefore exciton binding energy ($E_b = E_g - E_{1s}$) is not so easily discerned by an absorption spectrum alone. In the process of electroabsorption, an external electric field is applied to the sample which alters its absorption spectrum. At each wavelength, this change in absorption due to the electric field is measured and the resulting so-called electroabsorption spectrum has a shape that allows for easy and precise measurement of the exciton binding energy and the band gap, and also allows for the calcualtion of the polarizability α and dipole moment μ of the excitons within the material. Measurements using this technique have allowed our collaborators to model the tunability of these properties and observe their strong dependence on one another in the subclass of materials known as 2D metal halide perovskites. A step-by-step guide on how to perform these measurements in our lab is given in the appendix.

Keywords: electroabsorption, absorption, perovskite, semiconductor, exciton, exciton binding energy, band gap

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Contents

Chapter 1

Introduction

1.1 Overview of 2D Metal Halide Perovskites

Metal halide perovskites are a material at the forefront of modern semiconductor physics research. Their applications in solar cell technology have been shown to yield higher efficiency than their traditional, silicon-based counterparts [1]. Additionally, the technology and methods used to fabricate perovskite materials are far less advanced than what is used to manufacture refined and doped silicon wafers [2]. This translates to a significantly lower cost of production. Because of this ideal combination of utility and affordability, interest in perovskites and their unique properties has steadily grown in the past several years.

Perovskites assume the ABX_3 crystal structure (see figure 1.1a). The fundamental units of this structure are layers made up of positively charged metal cations (B), such as lead or tin, surrounded by octahedrons of negatively charged halide anions (X_3), such as iodide or bromide. In between these layers, there are other, usually larger cations (A) situated in the gaps between the octahedrons [5]. The class of perovskites studied in our lab are called 2D hybrid organic-inorganic because rather than an expansive, uniform perovskite crystal structure throughout the

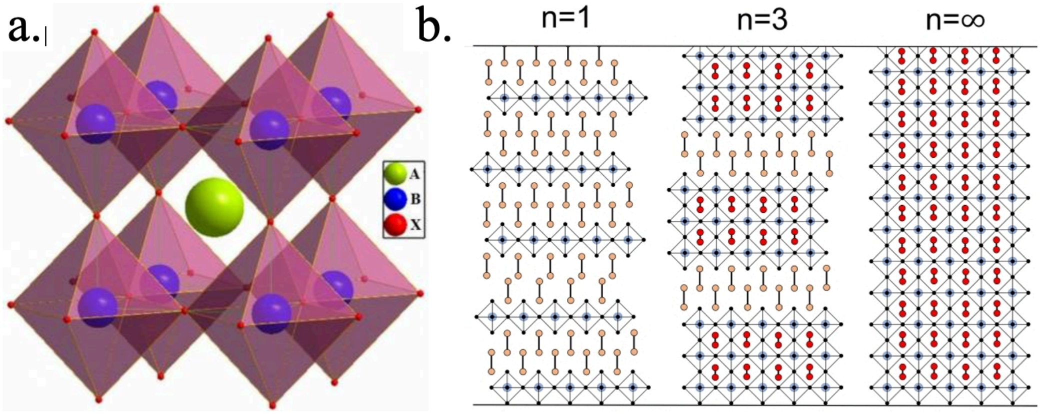


Figure 1.1 a. The ABX_3 crystal structure consisting of inorganic metal-halide octahedrons (BX_3) with anions (A) in the spaces between [3]; b. The pattern of perovskite dimensionality is demonstrated. The thin film perovskites we study are roughly 2D, meaning there are very few consecutive metal-halide layers before they are interrupted by the organic barrier molecules. [4]

entire material, our samples have individual (or a few) crystalline layers alternating with layers of an organic compound which takes the place of the "A" cation (see figure 1.1b). One thing that makes the perovskite structure special is that each of these building blocks—A, B, and X_3—can be substituted with other compounds resulting in significant changes to the opto-electrical properties of the material [6].

1.2 Important Measurements

Two such properties that are crucial to the performance of a semiconductor material are the band gap energy E_g and the exciton binding energy E_B. The band gap energy is the difference between the highest energy level of the valence band (VB) and the lowest energy level of the conduction band (CB) in a semiconductor. Typically, photons in the VB can be excited up to the CB where they can move freely, allowing for current to flow. When an electron in the CB drops back to the VB, it emits a photon having an energy equal to the band gap [7].

When an electron is excited to the CB, it leaves behind a region of net positive charge in the VB. This region is called an electron hole. Sometimes, an excited electron becomes bound to the hole that it left behind via electrostatic Coulomb attraction. When this occurs, the electron and its hole are said to form a quasi-particle called an exciton. When the constituents of the exciton recombine, meaning the excited electron falls back into the VB in the location of its hole, a photon is released. The energy of this photon is equivalent to the exciton's energy, usually denoted E_{1s}, and the difference between the exciton's energy and the band gap energy is called the exciton binding energy, denoted E_B. This energy is generally much lower than that of the band gap [8]. In semiconducting materials, E_g and E_B are very specific values which vary from material to material. They are also two of the most important properties to know because de-excitation of CB electrons and recombination of excitons are the main mechanisms for light emission in semiconductors [8].

1.3 Overview of Electro-absorption

Typically, measuring the two electrical properties mentioned in the previous section—E_g and E_B—is a matter of obtaining the material's absorption spectrum. This spectrum is obtained by shining a spectrum of various wavelengths of light through the material and measuring the intensity of the transmitted light at each wavelength. Absorption data can be calculated from this transmission spectrum. General excitonic and band gap features can usually be observed in the absorption spectrum, however, precise values of E_g and E_B are difficult to obtain with this data alone in non-theoretical samples (see figure 1.2). To address this issue, further absorption data is taken, this time with an AC electric field applied to the sample. This data is referred to as electroabsorption (EA) data. As will be explained in detail in this thesis, this field will alter its absorption spectrum in

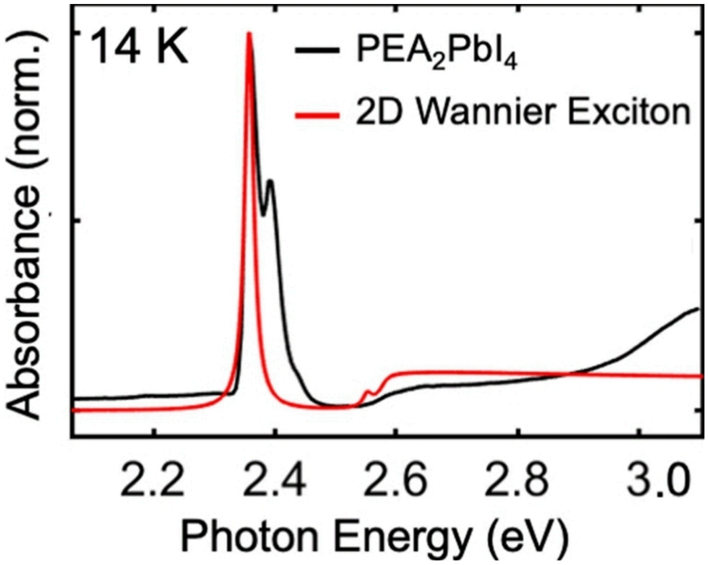


Figure 1.2 Theoretical absorption for phenethyl-ammonium lead-iodide (PEPI) is shown in red, while the real world absorption spectrum is shown in black. While the resonance peak in the lower energy region is clearly visible in both spectra, the theoretical step-like feature near the band gap (about 2.6 eV) is much more obscured in the real world absorption, making it difficult to estimate E_G based off of the absorption alone [9].

different ways depending on the type of states corresponding to each region of the spectrum. For bound states (excitons in the case of 2D perovskites), this shift will be according to both the linear and the quadratic stark effect, whereas for unbound states (free electrons in the CB), this shift will be according to the Franz-Keldysh effect [9]. It will be shown that if the difference between the original and shifted spectrum is plotted, the band gap feature is significantly more pronounced, and the exact values of E_g and E_B become much more precisely quantifiable [9]. The electroabsorption data can also be used to further characterize the sample's electronic properties, allowing for calculation of the dipole moment μ and the polarizability α of the excitons that form within the sample.

1.4 Thesis Outline

In the Colton research group at Brigham Young University, EA experiments are frequently performed on perovskite samples to measure their band gap and exciton binding energies as well as their dipole moment and polarizability. The goals of this paper are: 1) to establish the effectiveness of the electroabsorption technique in measuring these four values, 2) to describe the fundamental physics relevant to this experiment, 3) to give an overview of the equipment and methods necessary to carry out EA experiments, and 4) to present significant findings obtained through our group's collection of EA data over the past few years. For students wishing to perform these experiments using the facilities at Brigham Young University, a complete, step-by-step guide to do so is provided in the Appendix.

Chapter 2

Methods

2.1 Mathematical Description of Electro-absorption

The physical quantity referred to by electroabsorption is the change in the absorption of a material caused by the application of an external field:

$$\Delta A = A(F) - A(0). \tag{2.1}$$

We measure this value over a large spectrum of wavelengths, and the applied field causes different regions of the spectrum to change in distinct ways depending on the different particles contributing to the absorption in each region [10]. At lower energies, the absorption features largely depend on the breaking of excitonic bonds. At the higher end of the spectrum, its features mainly depend on the excitation of electrons from the valence band to the conduction band [10]. Therefore, the shift in the absorption spectrum in those energy regions depends upon the effect of an applied electric field on those respective particles (see figure 2.1).

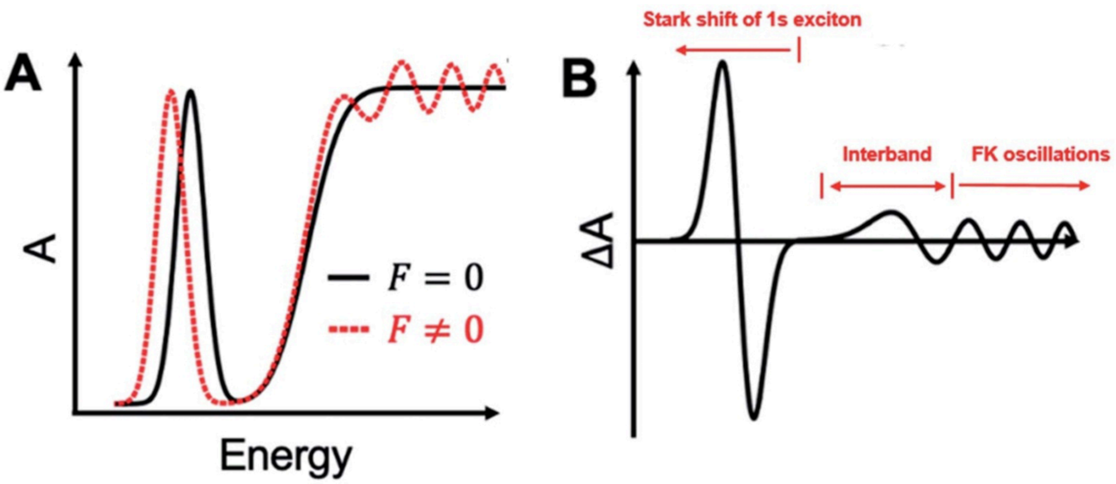


Figure 2.1 A. Cartoon representations of a semiconductor's absorption spectrum without an external field (black) and with an external field (red). When the field is applied, the exciton peak is uniformly red-shifted to lower energy. This is described by the linear and quadratic Stark Effect. Meanwhile the absorption in the band gap region appears to oscillate. This is described by the Franz Keldysh effect; B. The corresponding cartoon electroabsorption spectrum ΔA which is the change in absorption $A(F) - A(0)$ caused by the applied field [9].

2.1.1 Bound States

The excitons in the perovskites we study have binding energies that are significantly higher than the energy change that the applied electric field introduces. Because of this, the effect of that field on the excitons has been modeled using perturbation theory, and the associated change in energy has been described as:

$$\Delta E \propto -\Delta\mu F - \frac{1}{2}\Delta\alpha F^2 \tag{2.2}$$

where F is the strength of the applied electric field within the material, given by:

$$F = \frac{F_{applied}}{l} \tag{2.3}$$

where $F_{applied}$ is the voltage difference across the sample and l is the distance between the electrodes on the sample substrate, about 50 microns (see section 2.2.1) [10]. There is some disagreement in the literature as to whether this value for the field within the material should also be divided by the dielectric constant ε. However, because it appears less common to include ε when specifying the field, for the calculations performed in this paper, it is omitted. There are clearly shifts in the energy that go both linearly and quadratically with the applied field. These are called the linear (scales with F) and quadratic (scales with F^2) Stark shifts, and they are respectively proportional to $\Delta\mu$, the relative change in dipole moment, and $\Delta\alpha$, the relative change in polarizability, caused by the applied electric field. Since ΔE is assumed to be very small, we are free to approximate the EA signal using a Taylor series about ΔE: [10]

$$\Delta A = -\frac{\partial A}{\partial E}\Delta\mu F^2 - \frac{1}{2}\frac{\partial^2 A}{\partial E^2}(\Delta\mu F)^2. \tag{2.4}$$

Assuming the material is isotropic, $\Delta\mu$ will be oriented randomly. Therefore, in the first term where $\Delta\mu$ is multiplied by the field (which only points in a single direction), the entire term ends up averaging to zero. This leaves us with only quadratic field terms in the approximation. For the term proportional to $\Delta\mu F^2$, because $\Delta\mu$ is randomly oriented, the associated change in the absorption spectrum is called a “broadening.” This is because the affected electronic states will experience an energy shift according to the alignment of their electric dipole moment μ with the field, so some are shifted to higher energy while others are shifted to lower energy, causing the absorption spectrum in that area to broaden when a field is applied. [9] Excitons also experience a change in their absorption from an applied electric field due to their polarizability, $\Delta\alpha$. Because the dipoles created due to this polarizability are always aligned with the field, the change in energy due to $\Delta\alpha$ is always negative, meaning the absorption spectrum around the excitonic states is not broadened, but red-shifted uniformly to lower energy (see figure 2.1). This is known as the Stark shift due to the quadratic Stark effect, quadratic because it scales with the field squared.

2.1.2 Unbound States

The unbound states that are being probed in the electroabsorption experiment correspond to electrons that have been excited into the conduction band and are free to accelerate according to an applied

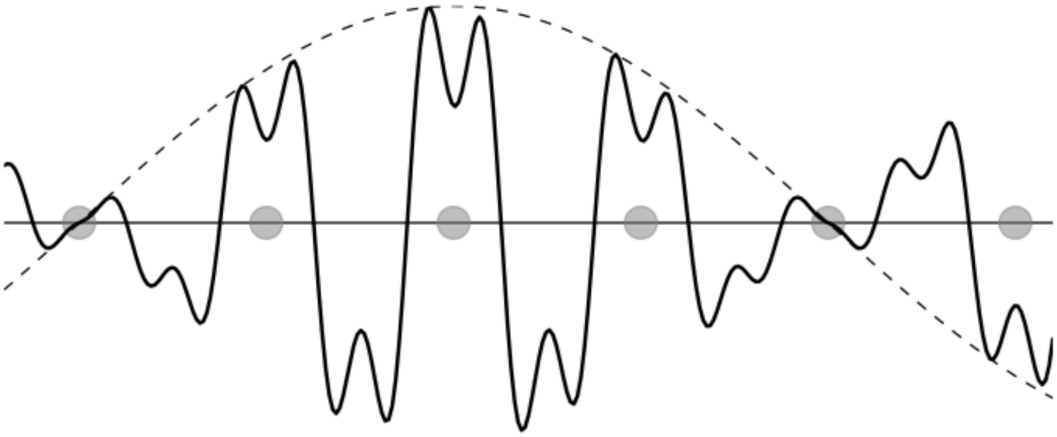


Figure 2.2 Because of the periodic potential within a crystal structure like a perovskite, the electrons in the conduction band (without an external field) have Bloch state wavefunctions. These are plane waves of a single frequncy modulated by the sinusoidal potential of the crystal structure [11].

external field [10]. The wavefunction Ψ of one of these electrons can be found by solving the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi = E\Psi \tag{2.5}$$

where the potential V is determined by the structure of the material. Because perovskites are crystalline, the potential can be approximated as sinusoidal, with maxima close to the atoms in the crystal and minima in between the atoms. This type of potential results in the wavefunctions taking the form of Bloch states [11] which are plane waves modulated by the sinusoidal potential from the crystal lattice (see figure 2.2). When an electric field is applied to the sample, however, a new term is introduced into the electrons' Schrödinger equation, which now looks like:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + (V + fx)\Psi = E\Psi \tag{2.6}$$

where V is the original potential from the crystal lattice, and fx is the energy from the field f [12]. The new solution to this equation reveals that the applied field has caused the wavefunctions

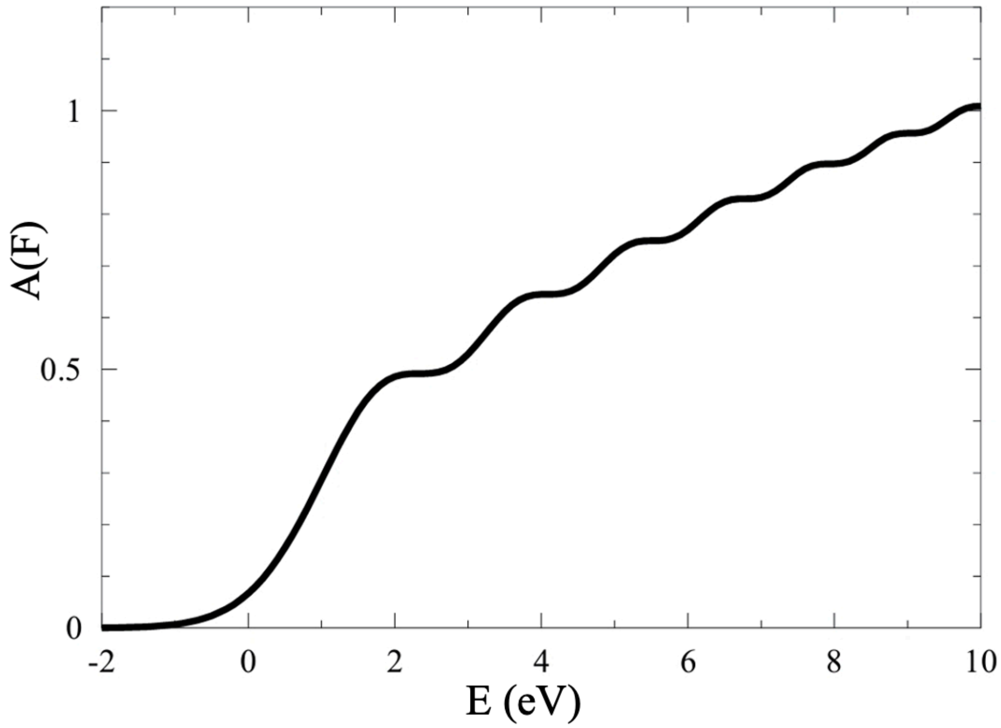


Figure 2.3 Oscillating absorption in the band gap region due to an applied electric field. This is an example of the Franz Keldysh effect [12].

to transition from Bloch states to Airy states [12]. This, in turn, causes the absorption spectrum in the band gap region (which corresponds to the free carriers in the conduction band) to increase by an Airy function (see figure 2.3). The derivation of this effect is well beyond the scope of this paper but is described in much greater detail in [12].

Considering the effect of this change in the absorption spectrum, it is clear that the EA spectrum in the band gap region (given by $A(F) - A(0)$) would simply appear as an Airy function, with oscillations near the band gap that damp out at higher energies. This is known as the Franz-Keldish (FK) effect (see figure 2.1). It is most rigorously described for bulk semiconductors ($n = \infty$, see figure 1.1) whereas the samples we study are generally 2D. Because of this, our samples demonstrate weakened FK oscillations which usually leaves only the first oscillation visible [10]. This is still extremely useful, as the first zero crossing of these oscillations is taken to be an accurate measurement of the band gap energy E_g [10], which is, again, one of the key properties to know for a given semiconducting material. It should be noted, however, that this assumption becomes less precise at temperatures much greater than 0 K. This is because the spectral line broadening, which can be thought of as uncertainty in the location of certain features in the absorption spectrum, increases with higher temperature [9].

2.1.3 Analyzing EA Data

The raw data generated during this experiment when we are measuring regular absorption (meaning absorption without an applied electric field) is actually transmission data, which must be converted to absorption data using the relation:

$$A = -\log_{10}(T). \tag{2.7}$$

Here, T is the absorption of the sample given by:

$$T = T_{sample}/T_{ref}, \tag{2.8}$$

where T_{ref} is the raw transmission data for a blank substrate without any sample coated onto it. When the electric field is applied, the raw data obtained is electrotransmission data ΔT, which is the difference in transmission due to the field:

$$\Delta T = T(F) - T(0). \tag{2.9}$$

To convert from ΔT to ΔA, we first divide equation 2.9 by $T(0)$ and then add 1 to both sides:

$$\frac{\Delta T}{T} + 1 = \frac{T(F)}{T}. \tag{2.10}$$

Then, recall that:

$$\begin{aligned} \Delta A = A(F) - A(0) &= -\log_{10}(T(F)) - (-\log_{10}(T)) \\ &= -\log_{10}\left(\frac{T(F)}{T}\right). \end{aligned} \tag{2.11}$$

From equation 2.10, we see that this is equivalent to:

$$\Delta A = -\log_{10}\left(1 + \frac{\Delta T}{T}\right). \tag{2.12}$$

There is an instrument correction factor to consider here which is due to the different ways that the signal might be modulated when measuring absorption vs EA, because the lock-in typically detects only the first or second Fourier components of the signal [13]. During our absorption scans, a chopper's frequency is used and during our EA scans, the frequency of the alternating electric field is used (see section 2.2.3). In our case, the modulations caused by both the chopper and the AC voltage end up resulting in neat square waves, so our correction factor γ works out to be extremely close to 1 and we are able to ignore it in our calculations of EA. However, if for example the AC voltage were in a sinusoidal rather than a square form, the correction factor γ would need to be calculated and included in the result for electroabsorption as:

$$\Delta A = -\log_{10}\left(\gamma\frac{\Delta T}{T} + 1\right) \tag{2.13}$$

It should be noted that the line shape rather than the amplitudes of the EA signal is important when measuring the band gap and the exciton binding energies. So, for those purposes it is occasionally sufficient to say:

$$\Delta A \propto -\frac{\Delta T}{T} \tag{2.14}$$

and just use $\frac{\Delta T}{T}$ in the analysis of those energy values (This works because the first term of the Taylor series expansion of $\log_{10}(x+1)$ is equal to $\frac{x}{\ln(10)}$). We obtain E_g by locating the zero crossing of the first oscillation in the band gap region of the plot of ΔA (see figure 2.1). Next, recall that E_B is obtained through the relation:

$$E_B = E_g - E_{1s}. \tag{2.15}$$

Once we have a plot of the regular absorption (no field), it is simple to find E_{1s}, the energy of the first excitonic state, by identifying the resonance peak (see figure 1.2). We then subtract this value from E_g to obtain the exciton binding energy [9].

It is also valuable to know the values α and μ for the excitons in a semiconductor, and using the data collected during the electroabsorption experiment, we are able to obtain measurements for them in addition to E_g and E_B. Looking at equation 2.4, we can rewrite it as [10]:

$$\Delta A = \frac{\partial A}{\partial E}\Delta E_Q + \frac{\partial^2 A}{\partial E^2}(\Delta E_L)^2. \tag{2.16}$$

where ΔE_Q and ΔE_L are given by:

$$\Delta E_Q = -\frac{1}{2}\alpha F^2 \ , \ \Delta E_L = -\mu F. \tag{2.17}$$

After the experiment is performed, we will have data for the EA spectrum ΔA and the regular absorption spectrum A. So, using that data, we fit the first and second derivatives of the absorption (obtained through computational methods) to the EA signal via a nonlinear regression according to equation 2.16. This results in numerical values for ΔE_Q and ΔE_L which can be used to solve for α and μ, respectively. The amplitude of the EA signal is important for this analysis, so it should be noted that $\Delta A \propto -\frac{\Delta T}{T}$ is not an appropriate substitution for ΔA in this case.

2.2 Lab Equipment

2.2.1 Sample Substrates

The perovskite samples are spin coated onto quartz substrates inlaid with gold interdigitated electrodes (IDEs). These IDEs are essentially two gold combs that face one another and have their teeth interlocked (but not touching) [figure: IDE]. When a potential is applied across the two electrodes, this geometry allows for an extremely even electric field in the plane of the sample throughout the region where the alternating teeth are.

Figure 2.4 An interdigitated electrode substrate similar to the ones our samples are grown on. The structure of these substrates allows for a very even field to be present in all parts of the sample over the fingers when a voltage is applied across the two main electrodes running vertically on either side [14].

2.2.2 Lamp, Spectrometer, and Detector

Our lamp provides white light with a continuous spectrum from around 300 nm to 900 nm. The light from this source is passed through as spectrometer, also called a monochromator, which has a diffraction grating that separates the light into its component wavelengths. These are then selectively transmitted according to the spectrometer's setting. This allows us to record transmission/absorption data for a large spectrum rather than a single wavelength of light. The spectrum can also be tuned to be as wide or narrow as we like within the upper and lower limiting wavelengths of the spectrometer.

2.2.3 High Voltage Source and Chopper

Fundamental to the electroabsorption technique is the application of an external electric field to our samples. This is accomplished by connecting the electrodes on the IDE substrates to an AC high voltage generator, which amplifies the signal from a function generator. The function generator outputs a frequency (983 Hz in our case) that, by design, is far from any of the harmonics of the common signals in the room (i.e., 60 Hz, 120 Hz). This is to allow the lock-in amplifier to pick out the electrotransmission signal from the noise in the room. When measuring regular transmission, the reference frequency sent to the lock-in (334 Hz in this case) is also sent to a chopper which is a disk that spins at a specified frequency with periodic holes to allow for light to pass through. This "chops" the light from the spectrometer into a square wave whose frequency is picked out by the lock-in resulting in much less noise in the absorption data.

2.2.4 Lock-in Amplifier

The lock-in amplifier is a device used extensively in experimental physics. Often, signals that scientists want to measure are simply too weak when compared to the surrounding noise for detectors to distinguish between the two. The lock-in is able to overcome this by picking out the component of the total signal that corresponds to a very specific, user-defined frequency. Relying on the principle of orthogonality of sine functions of different frequencies, the lock-in essentially integrates over the signal multiplied by a sine function with the frequency of interest. All other frequency components are cancelled out because of orthogonality and the result is the component of the signal corresponding to the reference frequency [15].

In the electroabsorption experiment, to ensure that the signal of interest is at a known frequency, the same signal used to produce the AC voltage by the function generator is passed into the lock-in amplifier as the reference frequency. In the sample, the field is alternating from on to off at the reference frequency. This switch occurs thousands of times over the course of the dwell time, which is the amount of time taken by the lock-in to record each individual data point before incrementing the wavelength to the next step. During each measurement, the detector is measuring the transmission of the sample and sending that data to the lock-in which, after extracting the proper frequency component, returns the average peak to peak difference of that filtered signal. This is equivalent to the average difference in the transmission value with and without an electric field applied, or $\Delta T = T(F) - T(0)$. This so-called electrotransmission data ΔT is converted to electroabsorption data ΔA using the methods described in section 2.1.3.

In the case of regular absorption where the chopper is used as the reference frequency rather than an AC voltage, the peak-to-peak difference measured by the lock-in is simply equal to the combined transmission of the sample and the IDE substrate, because the bottom peak of the square wave occurs when the chopper is blocking all light from reaching the sample.

2.2.5 Vacuum and Cryostat

Most of our 2D perovskite samples are extremely susceptible to oxidation when exposed to air, so it is necessary to isolate them from the atmosphere by vacuuming them down. Also, when using high voltage to probe a sample, air present around the digits of the IDE can become ionized which allows for current to flow between the nearby digits of the IDE. This obviously ruins the integrity of the electroabsorption data, so the experiment is carried out at low pressure, on the order of 10^{-5} mbar which makes the air surrounding the sample sparse enough to prevent any electrical shorts.

Something else important to consider is that excitonic features become much more significant at lower temperatures where thermal energy is not nearly as likely to be high enough to break an exciton's bond [8]. This means it is desirable to measure the exciton binding energy at low temperature, relatively close to zero Kelvin.

To achieve this combination of low pressure and temperature, our samples are placed on a so-called copper "cold finger" inside of a chamber connected to a vacuum pump. The cooling is done by a closed-cycle helium cryostat which can reach temperatures as low as 15 K. Inside, there is also a heater controlled by a PID. Together, they can regulate the temperature to be anywhere from about 15 K to 300 K in case the user desires to test for temperature-dependent phenomena.

Chapter 3

Results and Conclusions

The Colton group often collaborates with other research groups outside of Brigham Young University who create samples for us to measure. One such collaborator, Kameron Hansen of the University of Utah, has been fabricating metal halide perovskite samples for us for years. By using the electroabsorption technique to produce accurate measurements of these many samples' band gap energies and exciton binding energies, we were able to assist in demonstrating the tunability of those values via chemical substitution as well as the correlation that exists between E_g and E_B in 2D metal halide perovskites [6].

3.1 Example Data Set and Analysis

Here, the process of analyzing the data for a single sample will be demonstrated using phenethyl ammonium lead iodide (PEPI) as our example. The goal is to obtain numerical values for E_g, E_B, α, and μ. This sample was spin-coated onto an IDE substrate at the University of Utah then sent to the Colton lab for its transmission and electrotransmission to be measured. This was done using a spectrum from 420 to 570 nm (2.18 to 2.95 eV) and a voltage of 500 V. The absorption and electroabsorption spectra were then calculated using the equations laid out in section 2.1.3

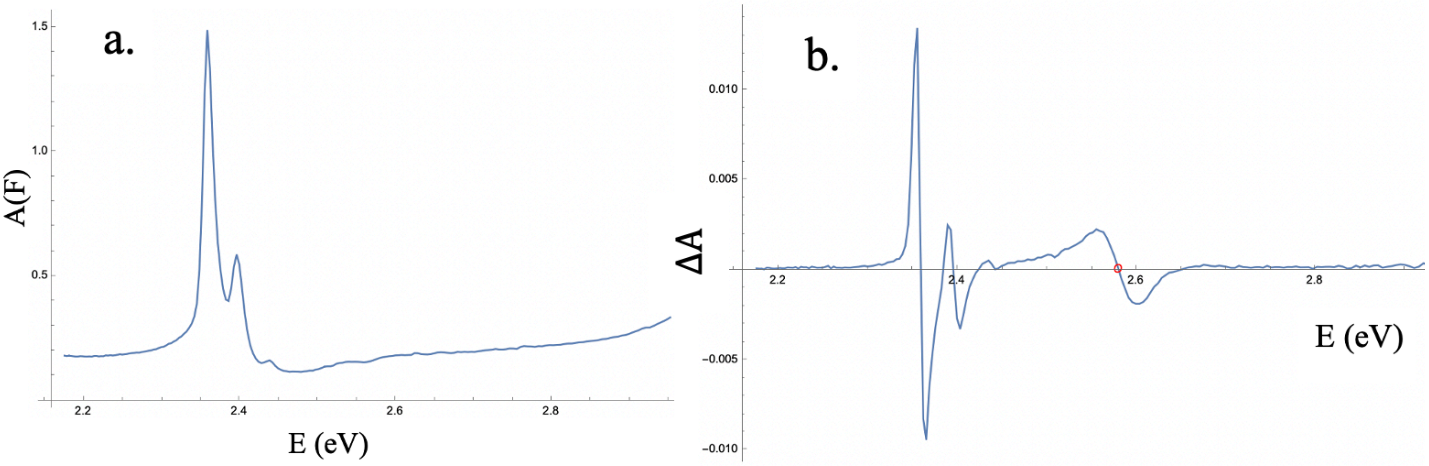


Figure 3.1 a. The absorption spectrum for PEPI. Notice the clear resonance peak at 2.36 eV indicating the location of E_{1s}; b. The electroabsorption spectrum for PEPI. Notice the first zero crossing of the Franz Keldysh oscillations is circled in red. The energy at this point, 2.58 eV, is an accurate measurement of the band gap E_B.

and have been plotted in figure 3.1. The exciton resonance peak E_{1s} in the regular absorption spectrum was found to occur at 2.36 eV. The band gap energy, located at the first zero crossing of the Franz-Keldysh oscillations is found to be 2.58 eV. Subtracting E_{1s} from E_g, the exciton binding energy for this sample is calculated to be 0.22 eV.

To calculate the polarizability α and dipole moment μ of the excitons in this sample, I computed the first and second numerical derivatives of the absorption spectrum with respect to energy. These derivatives were fit to the electroabsorption data (figure 3.2) according to equation 2.16. The fit (performed in Mathematica) returned fit parameters $C_1 = 1.07 \times 10^{-4}$ eV and $C_2 = 9.8 \times 10^{-10}$ eV. These values are respectively equivalent to ΔE_Q and ΔE_L which are defined by equation 2.17. To solve these equations, it must be noted that F refers to the field inside the material (equation 2.3, not simply the applied voltage across the sample.

While the SI units of polarizability are $C{\cdot}m^2{\cdot}V^{-1}$, it is more traditional to express α as a "polarizability volume" with units of $\mathring{A}^3$. Similarly, although the SI units of dipole moment are

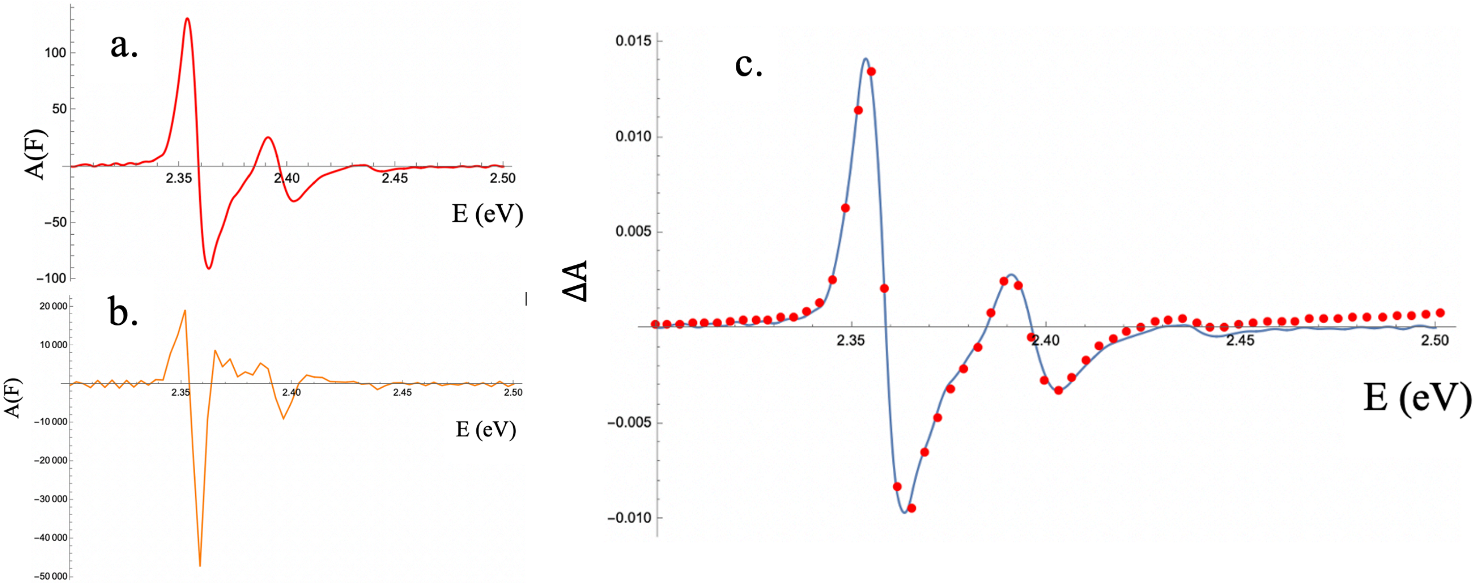


Figure 3.2 a. The first derivative of the absorption spectrum of PEPI, $\frac{\partial A}{\partial E}$ in the exciton region, from about 2.3 to 2.5 eV; b. The second derivative, $\frac{\partial^2 A}{\partial E^2}$; A linear combination of the derivative spectra in a. and b. fit to the electroabsorption spectrum.

C·m, it is more traditional to express μ in units of Debye. Using C_1 and C_2, we obtain values for α and μ which are 2.148×10^{-18} eV·m^2/V^2 and 9.821×10^{-17} eV·m/V respectively. The appropriate conversion factor for α is 1.44×10^{21} Å^3·V^2/eV·m^2 and for μ we use 4.80×10^{10} D·V/eV·m. Applying these factors, we obtain a polarizability volume of 3092 Å^3 and a dipole moment of 4.72×10^{-6} D.

3.2 Chemical Substitutions in Perovskite Semiconductors

It is widely known that the dielectric background of a given semiconductor has a major role in determining the exciton binding energy of that material [6]. Other factors such as the reduced mass of the exciton μ_r and, in the case of 2D hybrid organic-inorganic perovskites, the length of the organic barrier l_b also have their own effect on E_B. Each of these values can be altered via substitutions that change the chemical makeup of the perovskite crystal or the organic barrier

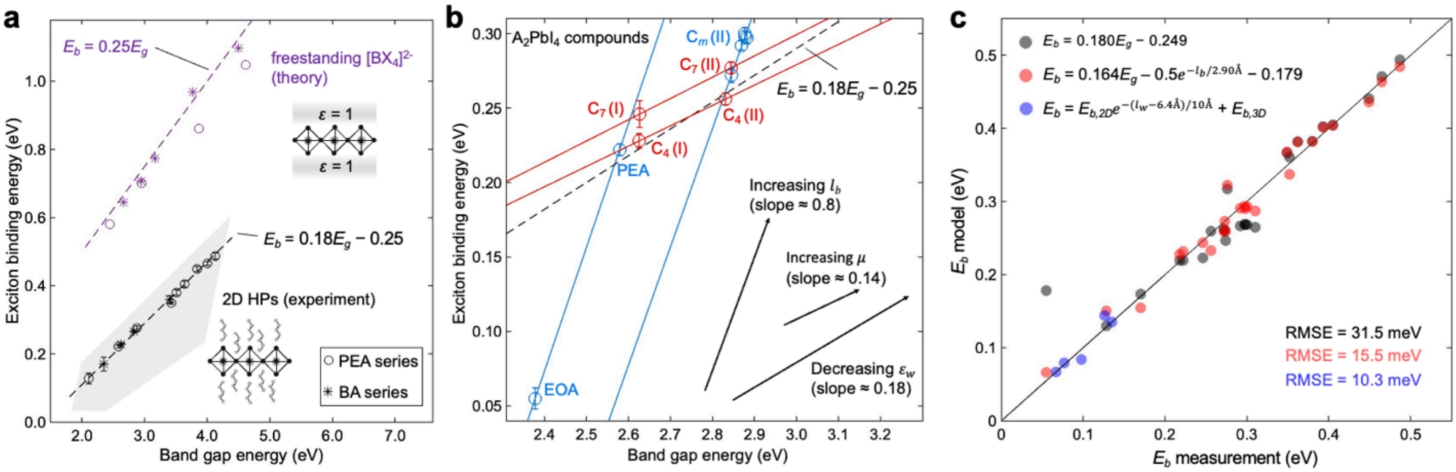


Figure 3.3 The results of a study of the band gap and exciton binding energy of 31 perovskite compounds conducted by researchers at the University of Utah and Brigham Young University. In b., three linear relationships between E_g and E_B are shown. Each has a distinct slope depending on which parameter-l_b, ε, or μ_r-is being manipulated [6].

molecules. For example, replacing iodine with a smaller halogen such as bromine or chlorine directly lowers the dielectric constant. Another parameter that was manipulated was the dimensionality of the hybrid organic-inorganic perovskites, using samples with $n = 1,\ 2,\ 3,\ 4$ and $n = \infty$ (see figure 1.1). In a recent study conducted by Hansen et. al., the electrical properties—including E_B, E_g, ε, μ_r, and l_b—of 31 different perovskite compounds were examined. The electroabsorption and dielectric data used to complete the study was obtained in the Colton lab over the previous three years, a good portion of which I was able to assist in collecting. The results of the study are plotted in figure 3.3, showing the various linear relationships between E_B and E_g depending on the internal characteristics of the perovskite that are being manipulated.

3.3 Combined Data and Analysis

The major results demonstrated by this data are the linear relationships that appear to exist between E_B and E_g when using chemical substitutions to alter specific material characteristics. When either the barrier length, the dielectric constant of the crystal, or the reduced mass were changed independent of the other two properties, it resulted in a linear adjustment to the exciton binding energy versus the band gap energy, though the slope of this linear relationship was distinct for changing ε, μ_r, or l_b. Another important result established by the study was that E_g is not strongly dependent on temperature, but rather is an intrinsic property of a perovskite's particular chemical structure [6]. This is the first strong correlation of E_g and E_B to be observed in 2D MHPs [6]. Because the various values of E_b seen in the data were obtained through direct chemical substitution, this suggests that, through these methods, both E_g and E_B can potentially be precisely tuned, making 2D perovskites an even more powerful and versatile material for use in semiconducting devices [6].

Appendix A

Electroabsorption: Step-by-step Instructions

A.1 Preparing the Cryostat

1. Make sure the cryostat is raised up with enough clearance below to remove the chamber cover. Tighten the hose clamps at the higher position to keep it in place.

2. If the cryostat is still vacuumed out, you won't be able to remove the chamber cover from the cold finger. As long as it has returned to room temperature already, you may vent the system by slowly opening the valves to allow air back into the vacuum area. DOING THIS AT LOW TEMPERATURE WILL DAMAGE THE CRYOSTAT!

3. Once the system has been vented, you can remove the cryostat chamber from the cold finger by twisting and pulling down firmly. When it is loose, carefully lower it straight down so it doesn't bang into the cold finger, then set it aside.

4. IMPORTANT! Many of our perovskite samples contain hazardous materials, including lead. Also, contact with our skin can contaminate the samples. In all steps requiring handling a sample, WEAR GLOVES!

5. If there is a previous sample glued to the cold finger, remove it by doing the following:
    (a) Turn on the soldering iron and wait until the green light flashes, indicating it is at the proper temperature.
    (b) De-solder the wires of the cold finger from the electrodes, making sure the wires don't get solder on the sample when they detach. The best way to do this is to hold the wire with tweezers, pulling gently away from the sample while heating the solder with a soldering iron in the other hand.
    (c) Remove the GE varnish gluing the sample to the cold finger. To do this, take a razor blade and slice underneath the sample gently from all sides until the sample is loose enough to remove by hand. DO NOT PRY OR PUSH WITH THE RAZOR BLADE OR THE SAMPLE WILL BREAK! SLICE ONLY!!
6. If the old sample needs to be used in the future, IMMEDIATELY vacuum seal it with the Vac 750 located against the wall facing computer 1.
7. Clean off the old GE varnish residue by first scraping it off with a razor blade, then wiping the cold finger's surface with a cotton swab wetted with isopropyl alcohol located in the optics supply cabinet facing computer 2.

A.2 Applying the New Sample

8. Remove the new sample from its sealed container and test its resistance with the blue Omegaette multimeter, connecting the multimeter's electrodes to the two electrodes on either side of the IDE and using the 2 MΩ setting:

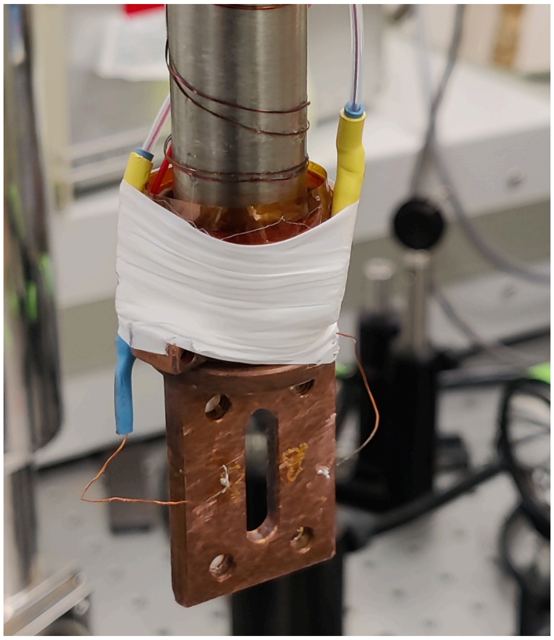


Figure A.1 The cold finger with its wires. The left wire goes to pin "B" and the right wire goes to pin "E".

  (a) If the multimeter directly reads the default 1 MΩ (with no decimal places listed), it means the resistivity is greater than 2 MΩ and the sample will be just fine with up to 600 V across it.
  (b) If the sample has low resistivity (less than 1 MΩ) it may experience dielectric breakdown when exposed to higher voltages, so the maximum voltage throughout the experiment should be lowered to avoid damaging the sample.
  (c) If the resistivity is 0 or close to 0, it means there is most likely a short. If so, you can look at the sample under a microscope and attempt to remove any objects (usually bits of solder) that are making an electrical connection across two of the fingers of the interdigitated electrode substrate. This “sample surgery” should be done with a precision razor blade with a skinny tip. Barely any force needs to be applied.

9. Once you know the sample has good resistivity, apply 2 small drops of fresh GE varnish on

either side of the hole in the cold finger, leaving about 2 mm of space between the drops and the edge of the hole. Make sure not to leave any trails/strings of adhesive that could obscure the sample during the experiment.

10. USING GLOVES, gently press the new sample onto the drops of varnish, such that the IDE's skinny teeth point horizontally, and the wide outer electrodes are oriented vertically, one on either side of the hole. The light for the experiment will pass through the center of the sample, so only press on the edges next to the electrodes to avoid contaminating/damaging the central part.

11. Solder the cold finger wires to the sample electrodes:
    (a) Make sure the electrodes are clear of any sample by scraping them gently to expose the metal. This will allow for a more secure solder.
    (b) Pick up a bead of solder by melting a little onto the tip of the soldering iron. Place it on the electrode, making sure not to cover any of the fingers of the IDE.
    (c) Holding one of the cold finger wires with tweezers, heat the solder on the electrode closest to that wire* with the soldering iron, place the wire in the solder, and remove the soldering iron, holding the wire in place with the tweezers until the solder hardens. Repeat for the other wire and electrode.

    *The left wire is connected to pin "B" and the right wire is connected to pin "E".

A.3 Testing the Solder

12. Make sure no new shorts have been introduced by testing the resistivity from one electrode to the next. It should be the same as before soldering. If it is zero, you shorted it! Remove the sample and perform "sample surgery" as explained in step 8c. Then resolder.

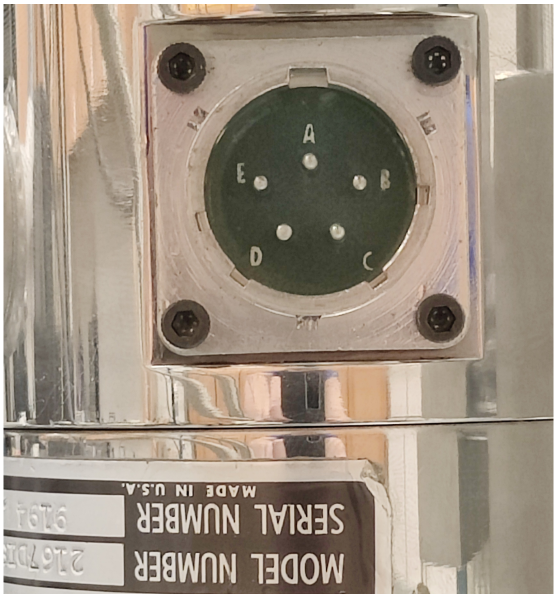


Figure A.2 Layout of the cryostat pins for applying voltage to the sample.

13. Using the multimeter, make sure that there is zero resistivity between the electrode on the left of the sample and the pin labeled "B" on the top of the cryostat. Next, make sure there is zero resistivity between the electrode on the right of the sample and the pin labeled "E" on the top of the cryostat.

14. Ensure there is NOT zero resistivity between pins "B" and "E".

15. If each of these tests pass, you are okay to carefully replace the chamber cover and begin vacuuming out the system, making sure the cold finger wires do not touch the walls of the cryostat. Remember that the two glass panels of the chamber should face the light source and the detector such that light can pass through the sample. ALSO, REMEMBER TO TURN OFF THE SOLDERING IRON WHEN YOU ARE FINISHED USING IT!

Figure A.3 The vacuum pump. Only ever touch the power switch and Auto Control System Start/Stop.

A.4 Vacuuming out the Cryostat

16. Seal the vent leading from the vacuum to the outside air, leaving the vent from the vacuum to the cryostat chamber open.
17. Turn on the vacuum by flicking the switch on the back. Wait for around 30 seconds for the device to finish its startup process, then press the button labeled “Start” under “Auto Control System”.
18. Allow the pump to reach a pressure of about 5×10^{-5} mbar, then you may seal the valve connecting the pump to the cryostat chamber. Once that is closed, you may turn off the pump

Figure A.4 The water line valve handles. Twist them so they both point up to open the valves.

by pressing the “Stop” button under “Auto Control System”. After this, wait between 5 and 10 minutes for the turbo pump to spin down and you may flip the switch on the back of the vacuum to power it completely down.

A.5 Setting the Temperature

19. Once the vacuum is at low enough pressure (about 5×10^{-5} mbar), if your experiment requires bringing the sample to low temperature, you should open the water cooling lines by twisting the two yellow valve handles high above the laser table next to computer 2. “Open” position is parallel to the pipe, “closed” position is perpendicular.

20. Next flip the orange switch on the helium compressor underneath the laser table where the cryostat is sitting. The helium pump should begin immediately.

Figure A.5 The helium compressor.

21. To set the desired temperature, turn on the PID temperature controller by flipping the switch on the front.

22. Click “Enter” until the desired digit (hundreds, tens, ones, etc.) is underlined. Then click “Scroll” to adjust the current digit to the desired value. Press “Enter” again to switch to the next digit. When you are finished setting the desired temperature, click “Return” to confirm and activate the temperature controller. To go to as low of a temperature as possible (usually 15 to 18 Kelvin) simply set the target temperature to 0 K.

23. If you are doing a temperature series, you will need to activate the temperature controller’s heater. To do this, press “Return” twice, or until the green light labeled “Heater” turns on. This will allow the PID to quickly go from low temperature to higher temperature. Note: The process of heating is significantly faster than that of cooling. So if you need to do a

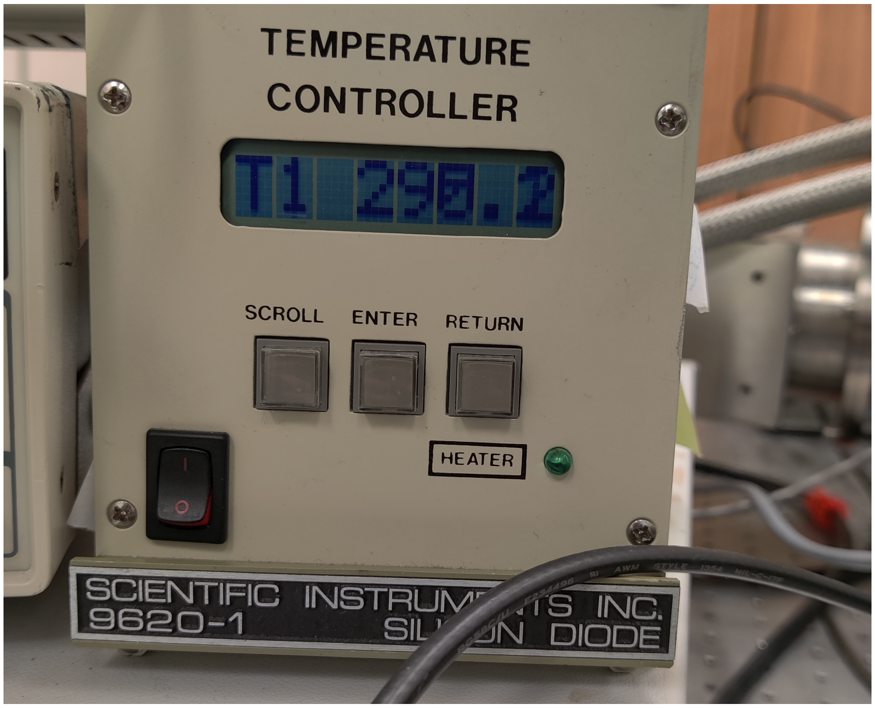


Figure A.6 The temperature controller.

temperature series, it is most time-efficient to begin with the lowest temperature in the series and then to perform scans in ascending temperature order. Also, when changing temperatures, make sure the temperature controller displays the target temperature for at least 5 minutes before beginning the new scan.

A.6 Scanning the Blank

24. Your sample data will need to be compared to the transmission of a blank substrate. To do this, keep the cryostat in the elevated position.

25. Turn on the SR830 (upper) lock-in amplifier by flipping the power switch on the back.

26. Turn on the Oriel Instruments lamp by flipping the orange power switch on the front, and

Figure A.7 The lock-in amplifier.

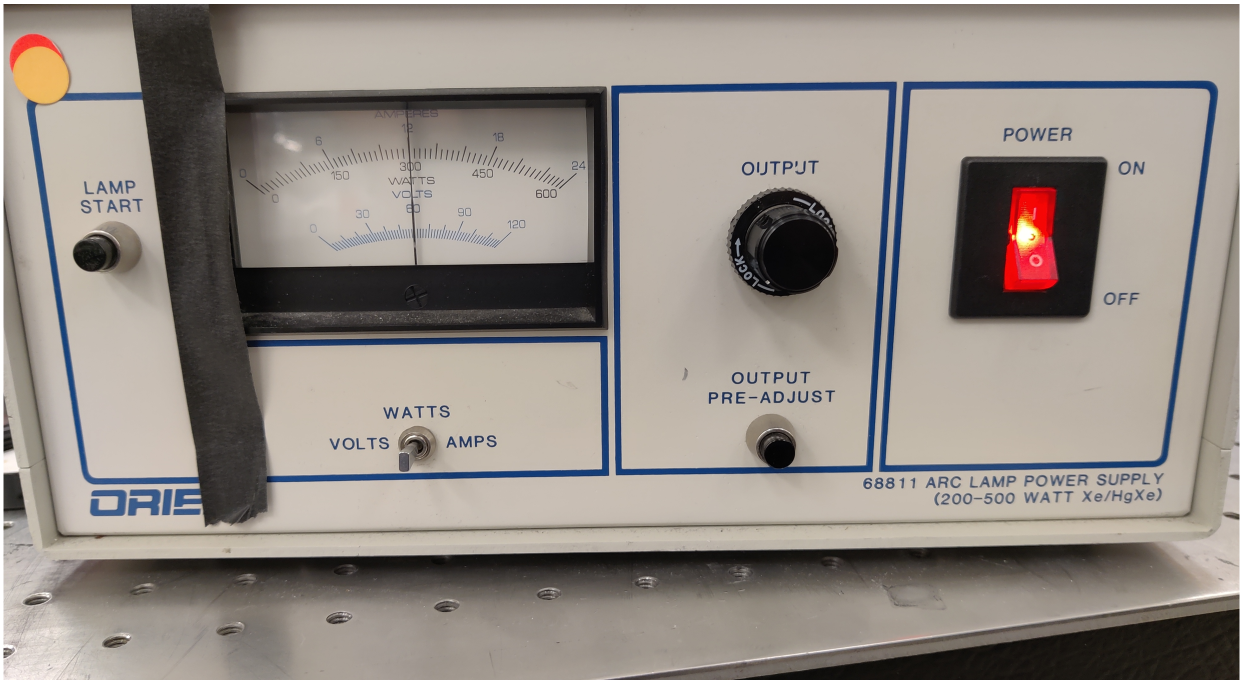


Figure A.8 The Oriel Instruments lamp control box.

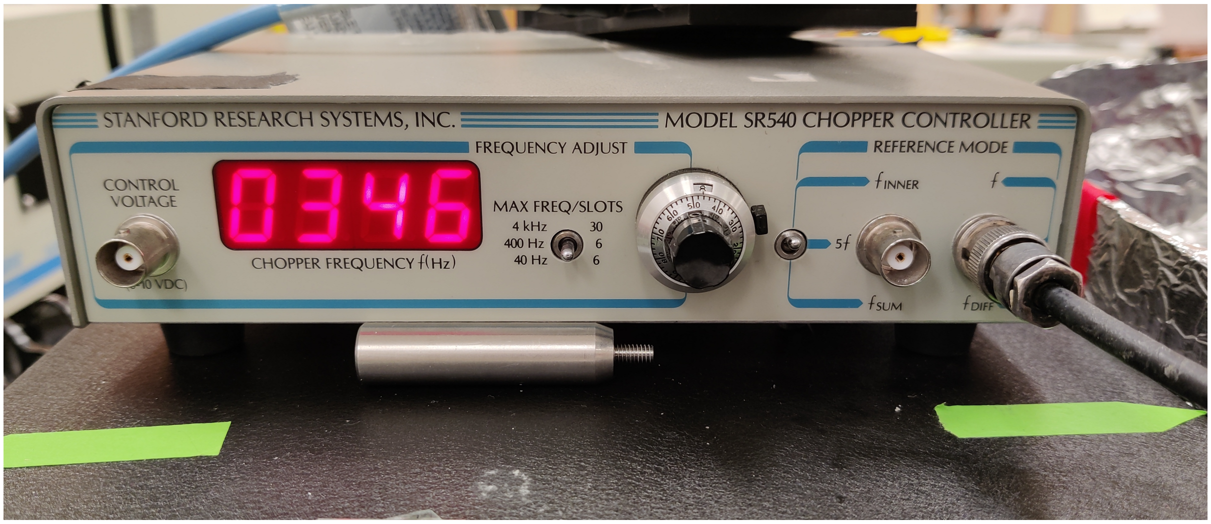


Figure A.9 The chopper's control box.

then holding down the "Lamp Start" button until the lamp turns on. Set the dial on the lamp's control box to 300 W.

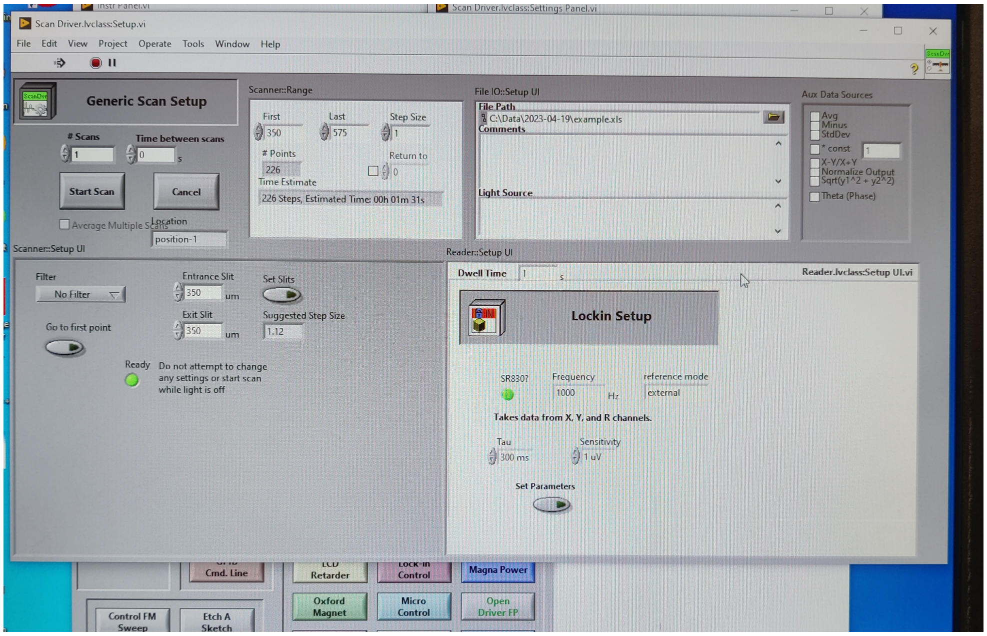
27. Turn on the chopper by flicking the power switch on the back of its control box. Make sure it is set to 345 Hz* by twisting the dial on the control box if necessary.

    *There is nothing especially significant about 345 Hz. It is just relatively fast and is not a multiple of 60 Hz (which is the base frequency of the rooms electronic noise). We use it to be consistent with previous scans.

28. Connect the rightmost BNC port of the chopper's control box to the SR830's "Ref In" port.

29. On computer 2, open the "Main.vi" file in LabVIEW located in C:\LabVIEW-programs\Main. Press "Run" (the arrow in the upper left) then click "GO".

30. Now, you are able to configure the settings for your scan. Start by naming your scan. Click on the button that looks like a folder next to the "File Path" box. Enter the name you want, in this case, "blank.xls". Note: For the first scan that you do in a day, you will have to manually add the ".xls" file extension, but all future scans will automatically include it. Notice also that



Generic Scan Setup
Scans: 1
Time between scans: 0 s
Location: position-1
First: 350
Last: 575
Step Size: 1
Points: 226
Return to: ☐ 0
Time Estimate: 226 Steps, Estimated Time: 00h 01m 31s
File Path: C:\Data\2023-04-19\example.xls
* const: 1
Filter: No Filter
Entrance Slit: 350 um
Exit Slit: 350 um
Suggested Step Size: 1.12
Ready ● Do not attempt to change any settings or start scan while light is off
Dwell Time: 1 s
Lockin Setup
Frequency: 1000 Hz
reference mode: external
Takes data from X, Y, and R channels.
Tau: 300 ms
Sensitivity: 1 uV

Figure A.10 This is the screen where you can adjust the parameters of your scan.

when you create the first scan in a day, a folder with today's date is automatically generated in the C:\Data folder and the file is saved there by default. Click "OK" to keep configuring the scan.

31. When setting up any scan, make sure the whole light beam is passing through the substrate. To do this, adjust the spectrometer to output a visible wavelength (like 530 nm) by typing the wavelength in nm into the "First" box towards the top of the page. Then click the "Go to first point" button on the left-hand side. The beam will now be very visible, and you can adjust the sample so the light passes through it. IMPORTANT: MAKE SURE ALL OF THE LIGHT FROM THE SPECTROMETER HITS THE DIGITS OF THE IDE SUBSTRATE!

32. Once you are certain everything is properly aligned and in place, you may set the "First" and "Last" boxes to be the beginning and ending wavelengths of the desired spectrum. YOU MUST USE THE SAME VALUES HERE FOR YOUR BLANK, TRANSMISSION, AND ELECTROTRANSMISSION SCANS OR YOU WON'T BE ABLE TO PROPERLY

ANALYZE THE DATA!

33. For blank and transmission scans, set the “Dwell Time” box to 1s and the “Tao” (time constant) box to 300ms. This isn’t strictly required, but it is typically the setting used. The strict requirement is that the dwell time be about 3 times the time constant no matter what scan is being performed. AFTER SETTING THE DWELL TIME AND TIME CONSTANT, YOU MUST CLICK THE “SET PARAMETERS” BUTTON IN THE BOTTOM RIGHT BEFORE RUNNING THE SCAN!

34. If there isn’t a lot of signal after a scan, the slit sizes can be increased. Typical slit size is 350 microns, and the “Exit Slit” and “Entrance Slit” should be set to the same size. Just remember that you must have the same slit size for the blank, transmission, and absorption scan for your data to be valid. After setting the slit size, click on the “Set Slits” button.

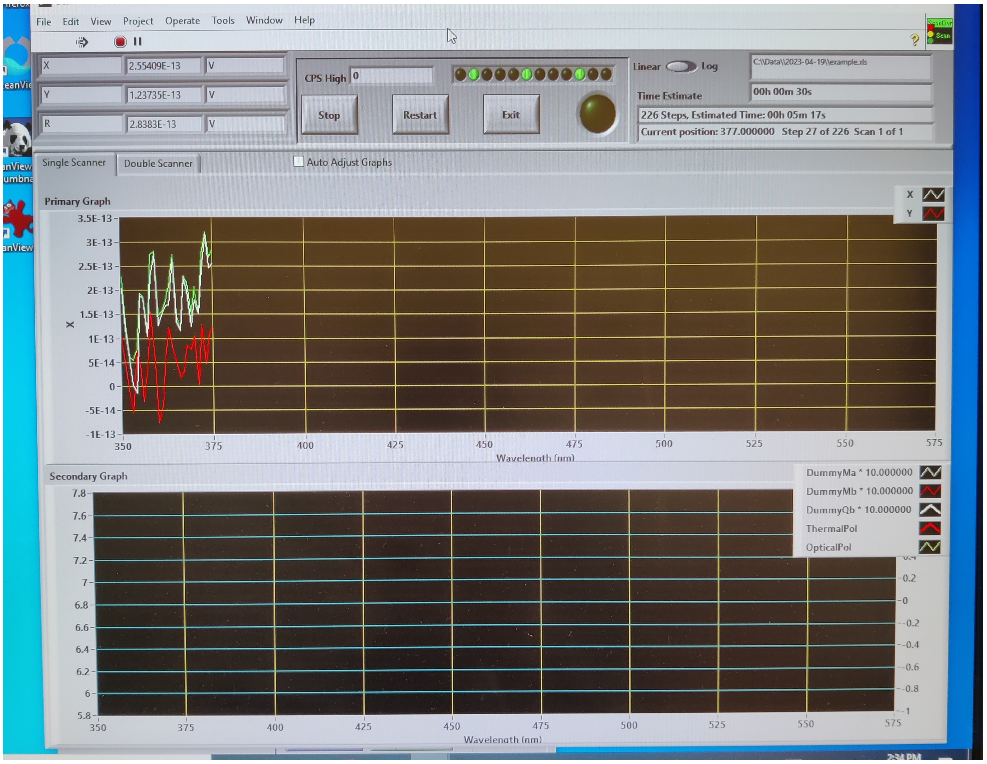
35. Now that all parameters are set, click on the “Go to first point” button. Wait for the “Ready” light to the right to light up. Turn the lights off and click the “Start Scan” button in the upper left of the page.

36. When the scan is done, the data will automatically be saved with the name you gave it in the folder with today’s date.

A.7 Transmission Scans

Note: The raw data we collect is actually transmission and electrotransmission data which is converted mathematically to absorption and electroabsorption data afterwards.

37. To measure a sample’s transmission, after the previous scan has finished, click “Restart” in the upper middle of the page. This will open a window where you can enter the name of the



X 2.55409E-13 V
Y 1.23735E-13 V
R 2.8383E-13 V
CPS High 0
Linear Log
C:\\Data\\2023-04-19\\example.xls
Time Estimate 00h 00m 30s
226 Steps, Estimated Time: 00h 05m 17s
Current position: 377.000000 Step 27 of 226 Scan 1 of 1

Figure A.11 This is the screen you will see while a scan is in progress. To go back to the settings screen when the current scan finishes, click "Restart".

new scan. (Once again, it will automatically append the “.xls” file extension. Click “OK” and you will return to the page where you can change the scan parameters.

38. Using the same process as in step 30, make sure the spectrometer is outputting visible light, then remove the blank substrate from the beam, loosen the hose clamps holding the cryostat up, and lower the cryostat SLOWLY until the entire beam of light passes through the digits of the sample’s IDE substrate. Tighten the hose clamps so the cryostat remains in place.

39. You should use the exact same parameters for the regular transmission scan as the blank scan. Just make sure if you adjusted the “First” wavelength to see the beam that you set it to what it was during the blank scan.

40. Make sure the lights are off and press “Start Scan”.

A.8 Electrotransmission Scans

41. To measure electroabsorption, we will no longer use the chopper as a reference. Turn it off, make sure the chopper blade is still and especially that ALL THE LIGHT FROM THE SPECTROMETER PASSES THROUGH ONE OF THE CHOPPER'S HOLES!

42. Turn on the oscilloscope using the button on the top. Its channel one and 2 should be connected to the red and blue outputs on top of the "John Ellsworth Box"*. Using the channel 1 and channel 2 "VOLTS/DIV" dials in the "VERTICAL" section, set both of those channels to 100 V. In the "HORIZONTAL" section, adjust the "SEC/DIV" dial until the oscilloscope reads "250 μs" in white on the bottom of the screen. Once the high voltage has been turned on (in a later step), use the channel 1 and channel 2 "POSITION" dials in the "VERTICAL" section to make sure the entire waveforms are in the screen, otherwise the "MATH" channel will not look right.

    *The "John Ellsworth Box" reduces the voltage coming from the voltage supply by a factor of 5, keeping the square wave output clean. This is because the supply only provides a clean square wave output at the relatively high voltage of around 500 V. When the box is connected to the voltage supply, we are able to send a clean square wave of as low as 100 V to the sample.

43. Turn on the function generator with the button in the lower right corner. Set the function generator to 983 Hz* by typing "983" and then pressing the down arrow button that says "Vrms/Hz". Connect the upper left BNC connection on the function generator labeled "SYNC OUT" to the "5V/50OHM" trigger input on the high voltage supply. Then Flip up the left switch on the high voltage supply labeled "AC ON".

    *Once again, there is nothing inherently special about this number. It is close to 50% duty

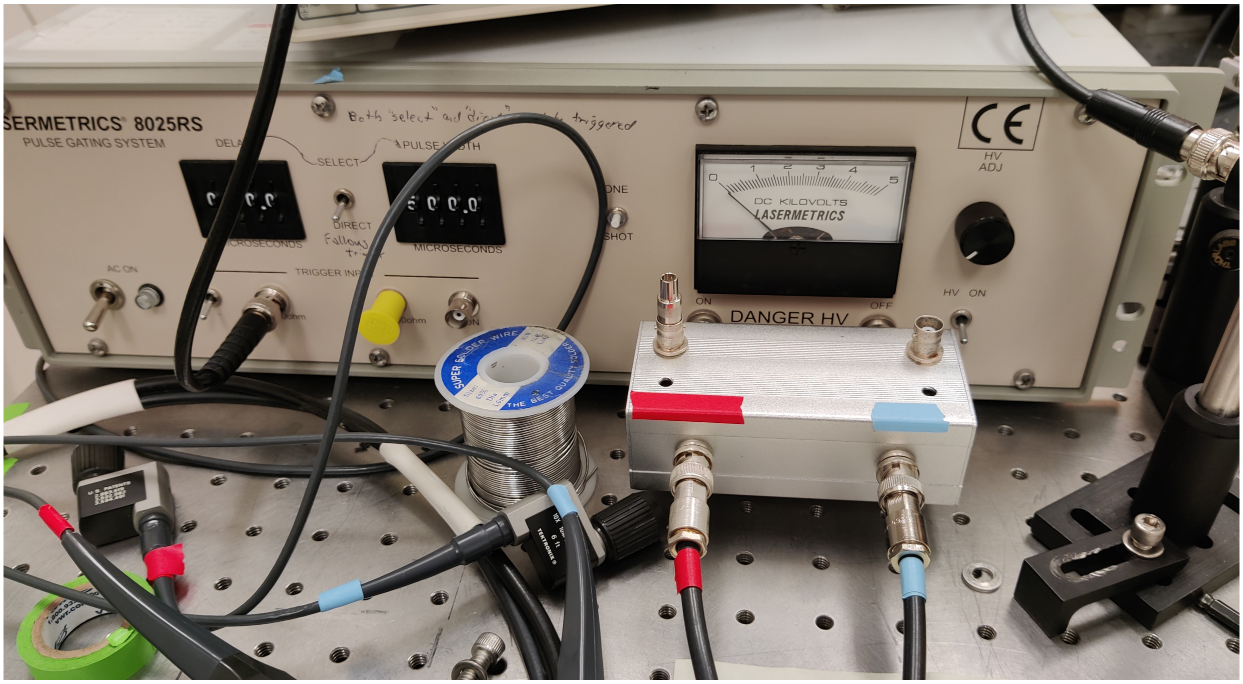


Figure A.12 The high voltage supply with the "John Ellsworth Box" attached to the front.

cycle, and we continue to use this frequency for consistency.

44. Remove the BNC cable going from the chopper box to the lock-in and reattach it from the BNC port on the bottom left corner of the function generator to the same “REF IN” port on the lock-in. This tells the lock-in to use 983 Hz as its reference frequency.

45. Plug in the 5-pin cable from the high voltage source to the top of the cryostat chamber, matching the appropriate letter pins to holes. Twist to secure the cable in place.

46. Now, click the “Measure” button on the oscilloscope. The red “MATH Pk-Pk” channel on the right side of the screen will read the voltage across the sample during the scan.

47. Make sure the switch in the middle of the voltage supply points downward toward “DIRECT”. Making sure the dial on the right of the high voltage supply is turned all the way COUNTERCLOCKWISE, flip the right switch on the high voltage supply labeled “HV ON”. Then,

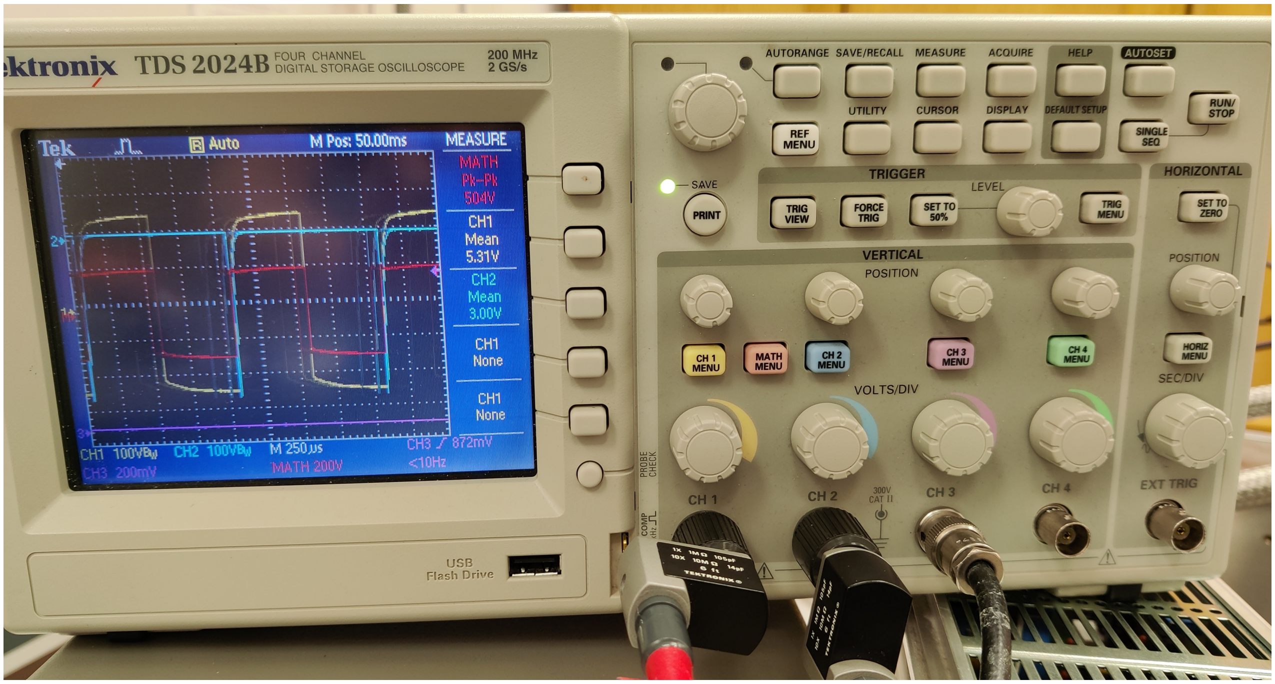


Figure A.13 The oscilloscope showing a square wave output (red channel).

slowly turn the dial clockwise until the “MATH Pk-Pk” channel reads the desired voltage. It should look like a square wave on the oscilloscope screen.

48. You are ready to set the parameters of your scan now. Click “Restart” on the previous scan’s page. A window will pop up for you to enter the name of your new scan. Click “OK” to continue setting the parameters.

49. Keep the “First”, “Last”, and “Entrance Slit” and “Exit Slit” parameters the same as in the blank and transmission scans.

50. Electroabsorption is usually a lot noisier than absorption, so change the dwell time to be 3 seconds and the time constant “Tao” to be 1 second. REMEMBER TO CLICK “SET PARAMETERS” AFTER CHANGING THE DWELL TIME OR TIME CONSTANT!

51. Turn the lights off and press “Start Scan”.

A.9 Finishing Up

52. When you are finished with all your scans, turn everything off including the chopper, the lock-in amplifier, the lamp, the function generator, the oscilloscope, the temperature controller, the high voltage supply (turn the dial all the way clockwise and both switches down), and the helium compressor.
53. After turning off the helium cooler, WAIT APPROXIMATELY 10 MINUTES before turning the valve handles for the water lines to the closed position (perpendicular to the pipe).

A.10 Other Notes

54. When performing a voltage series or a temperature series, make sure to perform both a transmission and an electrotransmission scan for each distinct voltage or temperature!
55. Some cell phones (especially iPhones with face ID) output a lot of infrared light when they are out of your pocket. Our detector is very sensitive to IR light and having such a phone out during a scan can result in excessively noisy data. Computer screens are usually fine, however.

A.11 Converting to Absorption and Electroabsorption

56. To convert the transmission data T to absorption data A, use equation 2.7:
57. To convert electrotransmission data ΔT to electroabsorption data ΔA, use equation 2.1.3:
58. These conversions can be quickly performed and visualized in Origin:

(a) Just copy and paste the wavelength and R columns of the blank scan into origin, then copy and paste the R column of the transmission scan next to them. Finally, copy and paste the "X" column of the electrotransmission scan next to them*. (At any point you can right click and select "Add New Column" to create more columns in Origin).

   *This is assuming the lock-in has been phased properly. If it hasn't, a linear combination r of the "X" and "Y" columns will have to be used given by

$$r = col(X) \cdot \cos(\theta) + col(Y) \cdot \sin(\theta) \tag{A.1}$$

   where the θ chosen maximizes the value of r. The group has developed code that performs this operation for us if necessary.

(b) Create two new columns, one for absorption and one for electroabsorption. Set the values of those columns by right clicking on them and clicking "Set Column Values".

   i. For Absorption, if the blank transmission column is named "blank" and the sample transmission column is named "T", set the absorption column equal to: "log(col(blank)/col(T))".

   ii. For electroabsorption, if the electrotransmission column is named "ET", set the EA column equal to: "-log(1+col(ET)/col(T))".

(c) Right click on any column and click "Plot" and its data will be plotted. Note that these plots will have wavelength (in nm) on the x axis. It is common to convert this to energy (in eV). To do this in origin, make a new column by right clicking on the column directly to the left of the "wavelength" column, then clicking "Insert". Double click on the newly created column, then change the "Plot Designation" to "X". Next, right click on the new column and click on "Set Column Values". Make the new column equal to "1240/col(wavelength)". Now, when you plot any of the data, it will be plotted versus energy in electron volts which is more typical for this type of data.

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