Abstract

Positronium annihilation lifetime spectroscopy (PALS) measurements are collected for four semi-crystalline polytetrafluoroethylene (PTFE) samples of varying permeability at room temperature using both a Bulk PALS and a Beam PALS apparatus. In addition, lifetime measurements in a temperature range of 20-160 °C were collected using the Bulk apparatus. Two collisionally quenched o-Ps lifetimes of approximately 1 ns and 4 ns are found in all samples, which correspond to Ps annihilation in the crystalline and amorphous regions of PTFE respectively. The relative intensities of the two o-Ps components are used as a measure for the samples’ crystallinity. The results of this experiment are used to characterize each of the four samples and correlations between the PALS results and the film’s permeability are discussed.
Acknowledgements

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1. Introduction

Polytetrafloraethalene (PTFE or Teflon®) was discovered in 1938 at DuPont when Roy J. Plunkett found that the tetrafluoroethylene gas he used in a study of chlorofluorocarbon refrigerants polymerized [1]. Plunkett realized this new material had a low coefficient of friction, and was resistant to heat and chemically inert. Today, PTFE is used in a variety of applications including coatings on non-stick cookware, stain protection for fabrics, environmental protection car finishes on cars, and nail polish [2]. PTFE membranes can be engineered so that they are impermeable to water but permeable to water vapor and smaller molecules, a technology which has been applied to breathable water resistant clothing and plays an important role in Proton Exchange Membrane (PEM) fuel cells. Varying void volume characteristics of these membranes, such as pore size and crystallinity would likely alter their permeability, thus permeability of these membranes is expected to be linked to their morphology [3]. Understanding the properties and structure of PTFE is essential for the improvement of existing technologies and the expansion of the uses of this polymer. The focus of this thesis will be the free volume characterization of semi-crystalline PTFE using Positronium Annihilation Lifetime Spectroscopy (PALS) with the hopes of correlating this with film permeability.

PALS is a well developed technique that has been employed for several decades for characterizing physical properties of polymers [4]. The PALS method non-destructively probes the open volume microstructure of complex materials and its function is not limited to open and interconnected porosity. It has wide use in describing
polymer features, including glass transition temperatures [5,6], temperature behavior and phase transitions [7], the effect of irradiation [8], and permeability [9,10].

PALS utilizes the reduced lifetime of ortho-positronium (o-Ps), the bound state of an electron and a positron, inside the voids of insulating materials to deduce the size and distribution of pores. The interaction of o-Ps within the voids’ walls reduces the positronium lifetime from the vacuum lifetime of \( \sim 142 \text{ ns} \) [11], and hence provides a direct measurement of the size of the pore in which the o-Ps annihilated. The fitted intensity of the Ps lifetime is used to provide information on the density of the specific sized pores.

In this experiment, the lifetimes’ relative intensities of the o-Ps within voids in the crystalline and amorphous regions of PTFE will be used to differentiate the samples’ crystallinity. The amorphous regions of semi-crystalline polymers arise from irregular packing of the polymer molecules (due to their large size, polymer molecules are easily distorted). Due to this inefficient packing, amorphous regions of a material have a larger free volume than purely crystalline regions. PALS is an ideal technique for differentiating between these amorphous and crystalline regions. Measurements in PTFE [6] found two distinct Ps lifetimes which correspond to annihilation in either the crystalline or the amorphous regions. The longer of the two lifetimes is due to Ps annihilation in the larger void volume in the amorphous phase while the shorter lifetime arises from annihilation in the smaller voids of the well-packed crystalline phase.

For this thesis we studied four thin PTFE films furnished by a well-known company in this field who contracted this work. At the present time concerns over proprietary information do not allow us to mention the company by name or any details
of the production processing. Despite these nuisances there is much to be learned about PALS in PTFE. The films are labeled 57, 4602, 147, and 59. The main difference in these samples is that they have different permeability to water vapor. Both 57 and 4602 have a thickness of 100 microns, sample 59 is 19 microns thick, and 147 is the thinnest sample studied, with a thickness of 10 microns. Each sample was assumed to have a density near 2 gm/ cm$^3$ which is a standard PTFE density. Two sheets of each material were provided, so the first sheet of each material is denoted by a -1 after the label and similarly, the second sheet is denoted by a -2 when appropriate. In addition, spectra are assigned as the front and back of each piece (here front and back are arbitrarily defined).

Two different PALS techniques were utilized to collect the data presented in this thesis, referred to as beam-based (Beam) PALS and Bulk PALS. These methods differ mainly in the method in which they implant positrons into the material; Bulk PALS being a direct deposition method while Beam PALS involves producing a controlled beam of positrons transported from the source to the sample. The positrons produced in Beam PALS are low energy (on the order of keV’s) which focuses attention on the surface of the film. These techniques have complementary advantages, and thus implementing both techniques has allowed us a more thorough investigation of our PTFE samples.

This thesis begins with a general overview of the PALS technique. Results obtained using the beam-based PALS are discussed in Chapter 3 while Chapter 4 contains the Bulk PALS results. Prior to the presentation of the data, Chapters 3 and 4 will also introduce the readers to the relevant PALS technique. Since the author was involved in the construction and operation of the Bulk PALS apparatus, discussion of the Bulk technique will be more in-depth. The thesis will conclude with a comparison of the
results obtained by the different techniques, call attention to apparent correlations between the films’ void volume characteristics and their permeability, and discuss future applications of PALS to the investigation of PTFE or PTFE containing films.
2. General PALS Technique

2.1 Lifetime shortening and correlation to pore size

When a positron (e^+) enters a polymer it may remain as a free positron or pair with an electron to form positronium (Ps), an unstable hydrogen-like atom. Like hydrogen, the ground state has two spin states, the spin singlet state (1^1S_0), called para-positronium (p-Ps), and spin triplet state (1^3S_1), ortho-positronium (o-Ps; unless indicated otherwise, Ps should be taken to mean o-Ps in this thesis). Their ground state (n=1) representations in Dirac notation are given below, where ↑ represents the spin of the electron and ↓ the spin of the positron.

\[ 1^1S_0 \quad |0,0\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \]  

\[ 1^3S_1 \quad |1,0\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \]

In vacuum p-Ps has a 0.125 ns lifetime [12]. Ortho-positronium is longer lived, with a vacuum lifetime of approximately 142 ns [11], due to spin-forbidden annihilation. However, in materials this lifetime is markedly shortened as a result of “pick-off.”
“Pick-off” annihilation refers to the process by which the o-Ps positron annihilates with an electron other than its bound partner as it collides with surrounding environment. To first order, the reduction of this lifetime in a solid depends on the rate at which the o-Ps interacts with molecular electrons. Naturally, the volume of the void in which the Ps is isolated (in order to minimize binding energy, Ps preferentially locates in voids or holes, where the dielectric constant is ~1) largely determines the rate at which these collisions occur. Thus, since the o-Ps reduced lifetime depends upon the rate of collisions, and the rate of collisions depends on the pore mean free path, the lifetime can be used to provide direct knowledge of the size of the pore in which it annihilated.

The calibration between measured lifetime and pore size was initially determined using the Tau-Eldrup (TE) model [13, 14] by treating o-Ps as a scalar particle with twice the mass of an electron confined to its ground state in a spherical potential well. In this model, the reduced lifetime of o-Ps trapped in a spherical pore of radius $R$ which is surrounded by an electron gas of an additional radius $\Delta R$ within which distance the o-Ps is assumed to annihilate with the spin-averaged lifetime of 0.5ns. The Ps lifetime in the pores, $\tau_{TE}$, is given by

$$
\tau_{TE}(R) = \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \right] \left( \frac{1}{\tau_S} + \frac{3}{\tau_T} \right)
$$

(3)

where $\tau_S$ and $\tau_T$ are the singlet and triplet vacuum lifetimes and $\Delta R$ is empirically determined [15] to be 0.16-0.17 nm. The TE model is sufficient for sub-nanometer pores. However, for larger pores it is necessary to include excited states of Ps in the well.
An extended Tao-Eldrup model, suggested by Goworek et al [16], that includes these excited states is used to calibrate the reduced lifetime into a mean pore dimension for larger pores. However, directly extending the TE model is extremely complicated due to the need to include high order Bessel functions and their zeros for an accurate result [16]. Since there is no compelling reason to choose any particular pore geometry (one can not know whether a pore is spherical, ovular, or any particular geometry), a rectangular pore is used to simplify the calculations [17]. Use of this extended Tao-Eldrup model is not strictly necessary for the pores in our PTFE samples, however, due to availability, this was the model used for calibration in this experiment.

2.2 Collecting and Fitting PALS Spectra

All PALS experiments (regardless of the specific apparatus used) are conceptually the same. Positrons are imbedded into a material where, within picoseconds, they thermalize and either annihilate directly or form either p-Ps or o-Ps. o-Ps may then annihilate with its natural lifetime or is quenched (quenching of p-Ps is negligible). A PALS apparatus uses a very fast timer to measure the time between the positron entering the material (the start) and the subsequent annihilation (the stop). A spectrum of decay lifetimes is generated by measuring on the order of a few million annihilations. A typical Ps annihilation lifetime spectrum, here for sample 147 at 110°C, is shown in Figure 1.
Several features are prominent in a PALS lifetime spectra including the prompt peak, a decay tail, and a constant background (Figure 1). The largest component of the prompt-peak is direct $e^+$ annihilation events; the resolution of the prompt peak is instrumental. The true feature of interest in the spectra is the decay tail, composed of $e^+$, p-Ps, and one or more o-Ps exponential lifetimes. The random background, apparent at long times, is due to uncorrelated annihilations. The specifics of the spectrum fitting depend on the PALS technique used. However, the goal is to extract two o-Ps lifetimes, corresponding to annihilation in either the amorphous or crystalline regions, and their associated intensities.
Two different fitting routines were used to analyze the positronium lifetime spectra, POSFIT [18] and LT9 [19]. The mathematical model of both POSFIT and LT9 considers a constant background added to sum of exponential lifetimes that have been convolved with an exponential sided Gaussian (ESG) resolution function. The prompt peak is simply a convolution of a Gaussian with an exponential on either side, $\tau^-$ on the left and $\tau^+$ on the right. Both of these programs perform a least-squares technique to extract the desired number of Ps lifetimes and intensities from the lifetime spectra. Each program, however, allows the user to control different fitting parameters and provides different fitting options. A thorough comparison between POSFIT and LT9 can be found in chapter 3.1.2.
3. Beam PALS

3.1 Introduction to Beam PALS

The first PALS technique we used is a beam of electrostatically focused positrons, called Beam PALS. The advantage of Beam PALS is the ability to control the positron energy, and thus the implantation depth of the incident positrons. This control of the positrons has several advantages, including the ability to investigate sub-micron films, depth profile, and study specific locations on a film's surface; thus making Beam PALS a powerful apparatus for investigating the surface properties of films.

3.1.1 Experimental Technique

A schematic of the positron beam used in this experiment is shown in Figure 2. Positrons are emitted during the $\beta^+$ decay of a 50 mCi $^{22}$Na source are implanted into a thin nickel foil (the moderator). The positrons are thermalized inside the moderator; due to nickel's negative work function (approximately 1 eV), a fraction of these ($\sim 5 \times 10^{-5}$) implanted positrons are thermalized and ejected back into the beam, from which point electro-magnetic lenses transport and focus the positrons toward the target chamber. Once inside the target chamber, the positrons travel towards the channel electron multiplier array (CEMA) plate where an applied voltage between the CEMA plate and sample repels the positrons into the sample. The energy of the positron is controlled by adjusting the lens voltages (for more details on the beam see [20,21]). For this
experiment, a beam energy of 5.8 keV was used, assuming a density of approximately 2 g/cm$^3$ for these PTFE films, this results in a mean implantation depth of about 230 nm.

Figure 2. Schematic of the Beam apparatus
Incident positrons may eject secondary electrons as they enter the sample. The same electric field that bent the positrons towards the sample now attracts these secondary electrons to the CEMA plate. The CEMA plate amplifies the electron signal which can then be converted into an electric pulse. This provides the start signal for a 4204 Lecroy time to digital converter (TDC).

The annihilation $\gamma$-photons are collected by the $\gamma$-detector, which consists of a four 5 x 5 cm pieces of fast plastic scintillator, each mounted to a photo multiplier tube (PMT). This detector arrangement allows a large solid angle for detecting the $\gamma$-photons, while preventing a degradation of the time resolution. The electric pulse from each of the PMTs is summed; this combined pulse serves as the signal to stop signal for the TDC. About one million decay events are collected in a 30 minute run and the timing spectrum is analyzed as described in chapter 2.

To check for lateral homogeneity within the 10 x 10 cm sheet, three pieces, approximately 1.5 cm square, from different corners of each sheet were used. Two sheets of each of the PTFE films were provided, so that six samples of each material were analyzed. In addition, a reference sample, a piece of film 147-1 was analyzed during each run as a test of reproducibility between runs. After being run once, the films were flipped so that the (arbitrarily determined) backside of the sample could be analyzed for comparison to the front side. For each run, six samples were mounted on the sample holder along with the reference sample and affixed inside the target chamber. The system was pumped down to approximately $10^{-7}$ Torr overnight. A lifetime spectrum for each of the six samples and one reference was then collected the following day.
3.1.2 Fitting the Beam Lifetime Spectra

A total of 48 lifetime spectra were generated on the Beam PALS apparatus. We fit these spectra to a prompt peak (which includes two exponential wings, $\tau_-$ and $\tau_+$, convolved with a Gaussian of width FWHM) and four lifetimes. The shortest lifetime ($\sim$0.1 ns) is due to positron annihilation in the film while the longest ($\tau \sim$90 ns) is due to positrons that backscatter from the surface and form high energy Ps. Neither of these components reveals information about the film porosity and are hence uninteresting. The two intermediate fitted lifetimes, around 1 and 4 ns, are due to Ps annihilating in the pores of interest.

Both the LT9 and POSFIT fitting routines were used in an effort to find the most robust fit. As discussed previously, LT9 and POSFIT use the same mathematical model, but they differ significantly in the degree to which the user can control the fitting parameters with regard to the prompt peak. POSFIT has been used extensively by the Michigan Positron Group and thus its operation is familiar [22]. LT9 however, allows the user more control over the fitting parameters and has been utilized for the analysis of semi-crystalline PTFE [5, 6].

POSFIT asks the user is asked to provide the number of exponential lifetimes and approximate values for each lifetime ($\tau$), the parameters of the resolution function (FWHM, $\tau_-$, and $\tau_+$), the time-zero position, and the constant background for a selected portion of the spectrum. The user has the option of letting the background and resolution be determined by the fit, or constraining them to the inputted values. One may also choose to fix any number of the exponential lifetimes and/or their intensities.
Since the $\tau^+$ exponential is on the same side of the Gaussian as the exponential decay tail, it is often difficult to separate the resolution function exponential from the short ~0.1 ns lifetime. While this lifetime is not of interest, fitting it incorrectly may have a strong systematic effect on the two intended Ps lifetimes. Since we have a reasonable estimate of the resolution function of the apparatus (from experience with data collected at the same beam energy) it can be beneficial to fix the value of $\tau^+$ to this estimated value to obtain less volatile fits. Unfortunately, using POSFIT, the user may only choose to fix the entire resolution function, not just $\tau^+$. LT9 however, does allow the user to fix the resolution parameters independently.

For the initial pass of the data on LT9, one simply selects the portion of the spectra to be analyzed and selects the parameters of the resolution function they would like to use in the fit. In the case of the PALS lifetime spectra, we activate the $\tau^-$ and $\tau^+$ exponentials. The estimated value of the FWHM is specified in the data file and does not need to be entered at the time of analysis. LT9 then fits the spectra and determines the number of lifetimes which yield the best fit. After the initial fit, the user has the ability to independently fix any of the fitting parameters used in POSFIT, or allow them to remain free; LT9 is then prepared for the final fit.

The procedure for producing the final fit is as follows: We fix the resolution function parameter $\tau^+$ to 0.158ns, the longest lifetime (due to backscattered Ps) to 90 ns, and the background as determined by POSFIT. The resolution FWHM and $\tau^-$ along with the remaining three lifetimes are then freely fit. We compared the $\tau_1$ (crystalline phase) and $\tau_2$ (amorphous phase) pore lifetimes fit by LT9 and POSFIT for consistency. Overall, the results were in excellent agreement, as expected. Given that the LT9 routine
constantly fit more robustly (i.e. the fitting tended to converge on reasonable results) and the greater degree of flexibility in the routine, we use the results from LT9.

As previously mentioned, the longest fit lifetime (fixed to 90 ns) is due to backscattering in the beam. Technically the backscattered Ps is not a single component, but rather a distribution of lifetimes. From experience, when the intensity of Ps in vacuum is small, we fit an additional 8 ns lifetime component, also due to backscattering. When fitting Beam PALS lifetime spectra, this 8ns backscattering component often mixes with the ~4 ns o-Ps component, thus artificially increasing its value. When fitting the PTFE spectra, we experimented with this additional backscattering lifetime. This lifetime was set to 8 ns and its relative intensity was varied over a reasonable range. Figure 3 demonstrates the effect that adding the 8ns backscattering component to the fitting parameters has on the $\tau_1$ and $\tau_2$ lifetimes and their corresponding intensities for sample 57-1. One can see that the impact of including this component on the lifetimes and intensities is trivial, and hence we will ignore it. The lifetimes extracted from the Beam PALS data should be considered a good estimate, instead we will focus on the relative intensities of the $\tau_1$ and $\tau_2$ lifetimes; more robust lifetimes are discussed in Chapter 4.
Figure 3. 57-1 fit with an 8 ns backscattering lifetime added at a variable intensity.
3.2 Beam PALS Results

Two Ps lifetimes were found in all of the samples. The shorter lifetime (~2 ns) is due to Ps annihilation in the crystalline regions, and the longer lifetime (~5 ns) in the amorphous regions (recall these lifetimes may be perturbed by the backscattering effect). The relative intensities of these lifetimes are used as a measure of the sample’s crystallinity. From this, the samples were divided into 2 groups. The high crystallinity samples, 59 and 4602, have lower (~7%) intensity in the amorphous lifetime, and thus a higher intensity in the crystalline Ps lifetimes than either 57 or 147. Physically, we would expect that the high crystallinity samples exhibit fewer disturbances that lead to large amorphous pores in their crystalline structure than the samples termed low crystallinity.

Since the Ps lifetimes were consistent between samples, those plots are uninteresting, and thus not provided. The plots of the intensities of these films are provided below (Figure 4-Figure 11), with the higher crystallinity samples appearing first. The labels on the x-axis labels refer to the particular sample analyzed. The first value refers to either sheet 1 or sheet 2 of the film (as does the second value in the sample label). A “b” designates analysis of what is arbitrarily called the back of the sheet. The samples from different sections of each sheet of material are referred to as 1st, 2nd, and 3rd.
Figure 4. 59-1 $\tau_1$ and $\tau_2$ intensities. The arrows indicate a possible front-back crystallinity difference.

Figure 5. 59-2 $\tau_1$ and $\tau_2$ intensities. The arrows indicate a possible front-back crystallinity difference.
Figure 6. 4602-1 $\tau_1$ and $\tau_2$ intensities. The arrows indicate a possible contamination effect.

Figure 7. 4602-2 $\tau_1$ and $\tau_2$ intensities
Figure 8. 57-1 $\tau_1$ and $\tau_2$ intensities

Figure 9. 57-2 $\tau_1$ and $\tau_2$ intensities
Figure 10. 147-1 $\tau_1$ and $\tau_2$ intensities

Figure 11. 147-2 $\tau_1$ and $\tau_2$ intensities
A few of these samples exhibited interesting surface features, sample 4602-1 (Figure 6) shows evidence of a possible contamination effect as indicated by a monotonic reduction in both Ps intensities, from the front to the back of sample. Since Ps intensity is affected by surface chemistry, it’s possible that a substance on the surface of the back side of the sample is responsible for this reduction. Less marked examples of a possible contamination effect can be seen in both sheets of the 147 films (Figure 10 and Figure 11).

Another interesting surface feature was found with sample 59. Both sheets of this film (Figure 4 and Figure 5) show evidence of a front-back difference in crystallinity. It is evident that this is not a contamination effect since the total Ps intensity of the sample remains constant. Instead, one can see from the following two figures, the amorphous Ps lifetime increases as the sample is flipped from the front to the back, whereas the crystalline Ps lifetime decreases. This shift is consistent with a change in crystallinity. A difference in the manufacturing method of this material may be the cause of this front-back difference in crystallinity.

Evidence of reproducibility with our fitting program and constancy with the beam operation is exhibited in the results from our reference sample, 147-1 (Figure 12). We can see that, with the possible exception of run “b5,” our results for the $\tau_1$ and $\tau_2$ lifetimes remained consistent.
Figure 12. 147-1 Reference Sample
In conclusion, the Beam PALS apparatus was able to illuminate interesting surface effects on several of the samples and to provide us with robust values for the intensities of the $\tau_1$ and $\tau_2$ lifetimes. These values are used to calculate the fraction of the sample in the crystalline state by dividing $I_1$ by the total Ps intensity ($I_1+I_2$), this is can be interpreted as a measure of the sample’s crystallinity (refer to the last column of Table 1). We can note from the results, summarized in Table 1, that the beam does not detect a significant difference in crystallinity between the thick 4602 samples and the thin 59 samples ($I_1/(I_1+I_2) > 0.6$), or between the thick 57 samples and the thin 147 sample ($I_1/(I_1+I_2) < 0.6$). Thus, the Beam PALS results suggest that the complementary thick and thin samples have the same crystallinity.

Table 1. Summary of the Beam results per sample. The value $I_1/(I_1+I_2)$ is used as a measure of the crystallinity of the sample, with a higher value meaning more crystalline.

<table>
<thead>
<tr>
<th>ID</th>
<th>$I_2$</th>
<th>$I_1/(I_1+I_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>±0.15%</td>
<td>±0.010</td>
<td></td>
</tr>
<tr>
<td>4602</td>
<td>7.00%</td>
<td>0.64</td>
</tr>
<tr>
<td>59</td>
<td>7.50%</td>
<td>0.604</td>
</tr>
<tr>
<td>147</td>
<td>9.00%</td>
<td>0.547</td>
</tr>
<tr>
<td>57</td>
<td>9.50%</td>
<td>0.527</td>
</tr>
</tbody>
</table>
4. Bulk PALS

4.1 Introduction to Bulk PALS

Unlike in Beam PALS, in Bulk PALS the source of positrons, in our case from $^{22}$Na, are implanted directly into the sample. The emitted positrons from $^{22}$Na have a range of energies up to 0.5 MeV, thus the implantation depth is uncontrolled. These high energy positrons penetrate deep into the sample, up to 500 $\mu$m (recall the mean implantation depth was 230 nm with the beam), and thus are probing the bulk of the sample.

The advantage of the Bulk PALS is the ability to provide an accurate value for the pore lifetimes. The Bulk apparatus has a better resolution function (which we are able to measure) and lacks the backscattering contamination present in the Beam apparatus. It also provides information on the pore sizes, and their distribution, for a larger volume of the film sample than does Beam PALS. However, Beam PALS provides robust values for the $\tau_1$ and $\tau_2$ intensities and only the Beam apparatus allows you to control the depth in which the positrons are implanted in the material, thus allowing the investigation of surface effects.

4.2 Apparatus and Technique

Our Bulk PALS apparatus evolved considerably before and during this experiment. This section discusses the changes made to the apparatus, including replacement of the $\gamma$-detectors and the redesign of the heating device, as well as a
description of the new “Wedge” configuration of the γ-detectors. The general method of Bulk PALS is also discussed.

Figure 13. A schematic of the Bulk PALS apparatus in the Normal configuration (as discussed in section 4.2.3)
The Bulk apparatus is relatively simple device, as shown in Figure 13. The mains components of the apparatus are the $\gamma$-detectors (discussed in Section 4.2.2) and the fast timing electronics that are required in order to precisely measure lifetimes on the order of nanoseconds. The signal to begin the lifetime measurement is the detection of the $1277 \text{ keV } \gamma$-photon that is released concurrently with the positron as the $^{22}\text{Na}$ source decays. The signal to stop the lifetime measurement is the detection of one of the $511 \text{ keV } \gamma$-photons produced when the positronium annihilates. The electric pulse created when a $\gamma$-photon is incident upon one of the detectors is sent to an Ortec 583 discriminator. The discriminator on the stop detector is set in windowed mode to accept pulses with an energy slightly greater than zero and less than $511 \text{ keV}$, and thus the signal produced by the $e^+e^-$ annihilation. The discriminator on the start detector is set to accept pulses with energy greater than $511 \text{ keV}$, thus the $1277 \text{ keV } \gamma$-photons produced by the source.

If a pulse from the $\gamma$-detectors falls within the range set by the corresponding discriminator, a pulse is sent from the discriminator to an Ortec 567 time-to-amplitude converter/Single-Channel Analyzer (TAC/SCA). The TAC measures the time between receiving a pulse from the start discriminator and receiving a pulse from the stop discriminator and generates a pulse with amplitude proportional to this time interval. If a stop signal pulse is not received in 50 ns, the TAC resets until it receives another start pulse. From the TAC the electronic signal is sent to an analog-to-digital converter (ADC)/ multi-channel analyzer (MCA), which translates the electronic pulses into digital numbers and sends them to the computer to be added to the cumulating lifetime histogram.
Nearly 300 lifetime spectra were generated on the Bulk PALS apparatus including both room temperature and heating runs. Once again, we fit these spectra to a prompt peak (which includes two exponential wings, $\tau_-$ and $\tau_+$, convolved with a Gaussian of width FWHM) and four lifetimes. However, these four lifetimes arise for different reasons than did the four lifetimes fit as described in Chapter 3. The two shortest lifetimes (~.125 ns and ~.4 ns) are due to p-Ps and positron annihilation (respectively) in the film. These components provide no information about the porosity of the films. The two long lifetimes, of order 1 and 4 ns, are due to Ps annihilating in the pores of interest. Once again the shorter of these two o-Ps lifetimes corresponds to annihilation in the crystalline regions of the film and the longer to annihilation in the amorphous regions.

4.2.1 Preparing the Sample

The source of positrons is created by evaporating tiny droplets of a salt water solution containing $^{22}\text{Na}$ (in the form of NaCl) on to one piece the each material. This process is repeated until the strength of the source is sufficient to collect one million events in roughly 30 minutes in the normal configuration, approximately 1 $\mu$Ci. The sample was then prepared by layering an equal number of approximately 1.5 cm square pieces of the material on either side of the deposited source, and then wrapping the bundle together in tin foil to hold the stack together and help contain the potential for any source leaking. Two thin pieces of aluminum were placed on either side of the sample packet, which is then placed in a small plastic bag for safe handling and storage. The purpose of the aluminum is to stop the highest energy positrons that penetrate the sample.
material before they reach the plastic bag or the scintillator of the detectors, where it would be possible for them to form Ps and annihilate, thus contaminating the signal.

To determine the thickness, i.e. the number of sheets required, of the sample needed to stop a majority of the positrons within itself, we collected spectra for thickness from one to nine layers (on each side of the source “sandwich”) of sample 57 (100 µm thick). The total o-Ps intensity (Ps formation fraction) as a function of the number of layers was plotted (Figure 14) for sample 57. The Ps intensity reaches a maximum of ~26.5% by 5 layers, which corresponds to a sample thickness of 500 µm. All bulk samples were then constructed to have at least this thickness, the thinnest sample, 147, used 50 layers per side, 59 used 25 layers per side, and both 57 and 4602 used 5 layers per side. One should note that for most of the samples, material from both sheets one and two were used, thus the additional -1 or -2 in the sample title is not relevant for the bulk data.

![Figure 14](image-url)

**Figure 14.** Positronium formation fraction of the number of layers of sample 57. 5 layers were required to stop nearly all of the positrons in the material of interest.
4.2.2 Improvements to the Apparatus

In an effort to improve the stability and time resolution of the Bulk PALS apparatus, the $\gamma$-detectors were replaced before the experiment. The $\gamma$-detectors are comprised of short cylinders of plastic scintillator mounted to the receiving end of Photonics XP2020 photomultiplier tubes (PMTs). The radius of the scintillator is equal to that of the PMT (25.5 mm); the height of the scintillator was 1 inch for the stop detector and 2 inches for the start detector. The scintillator was coupled to the PMT with optical coupling gel, and care was taken to ensure that the scintillator-PMT interface had a minimum amount of trapped air to reduce scattering of light. The detectors were then wrapped in several layers of electrical tape, to retain light and prevent electrical shock from the high voltage applied to the PMT. The gain was adjusted to produce pulses at a peak of 2 V on both PMTs (for more on adjusting the gain see Li Xie thesis [23]).

Once the new detectors were built, care was taken to select the appropriate limits for the start and stop discriminators. Incorrect discriminator settings can result in poor resolution, incorrect Ps intensities, and/or inefficient data collection. In order to ensure the discriminators were set to the optimal levels, we collected several discriminator curves, the goal being to allow the start detector to accept only the 1277 keV $\gamma$-photons emitted during the $\beta^+$ decay of the $^{22}\text{Na}$ source and the stop detector set to accept the 511 keV $\gamma$-photons produced during $e^+e^-$ annihilation. The lower level on the stop detector is set above zero to reduce noise and the upper level to reduce the number of Compton scattered 1277 keV $\gamma$-photons falsely accepted as annihilation events.

We first determined the optimal lower level of the start discriminator (LLD) (Figure 15) by measuring the Ps formation fraction within a polymer sample for LLD
settings from 200 to 1200 mV. A LLD setting of 1000 mV was chosen. Next the upper boundary of the stop discriminator was optimized (Figure 16) by selecting the ULD setting at which the derivative of the stop rate (with respect to the ULD) showed a drastic decrease. The LLD on the stop detector was set at 100 mV. In conclusion, the final settings for discriminators are 1000 mV for the LLD on the start detector and 100 mV for the LLD and 1400 mV for the ULD on the stop detector.

![Graph](image)

**Figure 15.** Ps formation fraction vs. the lower level discriminator (LLD) setting on the start discriminator. The optimal LLD setting was determined to be approximately 1000 mV.
4.2.3 Detector Configurations

Two different detector arrangements were used for the collection of the Bulk PALS data, referred to as Normal (Figure 13) and Wedge (Figure 17). The Normal configuration is the default set-up for the system. The detectors are both in very close proximity to the source, which enhances the rate of data collection. A typical coincidence rate for this set-up is on the order of hundreds of counts per second (cps). However, this close arrangement also makes it possible for the 1277 keV gamma photons to be Compton scattered from the start detector to the stop detector. If these Compton photons are less than 511 keV, then it is possible for them to trigger a stop event. These false stops contribute to the prompt peak and increase the intensity of the shortest lifetime, which in turn, decreases the intensity of the other components, primarily $\tau_1$ and $\tau_2$. 

Figure 16. Stop rate vs. the upper level discriminator (ULD) setting on the stop discriminator. The lines have been drawn in as a suggested fit. The optimal ULD setting was determined to be 1420 mV.
Compton scattering corrected intensities were calculated using

\[
I_{\text{corrected}} = I_{\text{original}} \left( \frac{100\%}{100\% - (I_{p-Ps} - 10\%)} \right)
\]

where \( I_{\text{original}} \) is the uncorrected \( \tau_1 \) or \( \tau_2 \) intensity (\( I_1 \) or \( I_2 \)) and \( I_{p-Ps} \) is the intensity of the short \(~125\text{ns}\) lifetime component that arises from p-Ps annihilation in the film. In the wedge configuration, the intensity of the positron annihilation component was typically 60\%, so thus the remaining 40\% should be composed of Ps annihilation events. Since we know that a quarter of Ps exists as p-Ps, we can conclude that \( I_{p-Ps} \) should be 10\% (one quarter of 40\%). This true value of \( I_{p-Ps} \) was subtracted from the Compton enhanced \( I_{p-Ps} \), typically around 30\%. This correction was subtracted from 100\% to find the corrected value for the total of the remaining intensities. All o-Ps intensities obtained in the Normal configuration were corrected by multiplying them by 100\% divided by the corrected value for the total remaining intensities.

The “Wedge” configuration, shown schematically in Figure 17, suffers from a greatly reduced rate of data collection (typically on the order of tens of cps) compared to the Normal arrangement. However the solid angle that would allow the Compton Scattering produced contamination is virtually eliminated. In the wedge configuration, the detectors are oriented at an angle, rather than face-to-face. A wedge shaped piece of lead is placed between the detectors to help prevent any direct Compton scattering of the \( \gamma \)-photons between them. The sample is then positioned at the end of the wedge, in an orientation that maximizes the coincidence rate.
To decrease the volatility of fits extracted from the data, $\tau^+$ was regularized as outlined in section 3.2.2 by fixing it to a measured value. $^{60}$Co, which undergoes $\beta^-$ decay, emitting $\gamma$-photons at 1.173 and 1.332 MeV was our primary source for the calibration. One lifetime, of approximately one picosecond was fixed in our fitting routine. The resulting fit resolution function is determined to be the actual resolution function of the system. The resolution function in each system was measured several times throughout the data collection process to ensure consistency in the systems and to improve our confidence in the measured resolution function. The values of the resolution functions’ parameters are dependent on the system configuration (Table 2).
Table 2. Typical parameters for the resolution function for each of the configurations used in the Bulk PALS experiment.

<table>
<thead>
<tr>
<th></th>
<th>(\tau^-) (ns)</th>
<th>FWHM (ns)</th>
<th>(\tau^+) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.085</td>
<td>0.250</td>
<td>0.120</td>
</tr>
<tr>
<td>Wedge</td>
<td>0.095</td>
<td>0.280</td>
<td>0.100</td>
</tr>
<tr>
<td>Heating</td>
<td>0.095</td>
<td>0.240</td>
<td>0.150</td>
</tr>
</tbody>
</table>

4.2.4 Heating Apparatus

To investigate the physics that occur in polymers at temperatures above or below room temperature, we sought to design cells for heating and cooling applications. A heating cell had already been used with the Bulk System to investigate glass transition temperatures in polymethyl-methacrylate (PMMA); however concerns about maintaining a sufficient mass for thermal stability led to a design that was inefficient for data collection and was incapable of cooling. Adding the ability to cool below room temperature would allow us to look for differences in the glass transition temperature \(T_g\); \(T_g = 195\ K\ [6]\) of the different PTFE samples. Since cooling posed a larger challenge than heating, the heating cell was redesigned as we investigated methods for cooling.

The previous heating cell (pictured in the left side of Figure 18) was cylindrically shaped. In order to accommodate the cell, the \(\gamma\)-detectors had to be separated by the diameter of the cell, about 6 cm with insulation. This distance reduced the solid angle for \(\gamma\)-photon detection, thus increasing the time required to acquire data. The improved heating cell (pictured on the right side of Figure 18) is a 8.3 cm x 7.6 cm x 2 cm rectangle, with the smallest dimension being along the vertical axis, thus reducing the required \(\gamma\)-detector separation to slightly less than 4 mm, while the larger dimensions in the horizontal directions still provide a large thermal mass to maintain thermal stability.
Figure 18. The only heating apparatus is on the left and the new apparatus is on the right. The new apparatus reduces the $\gamma$-detector separation by over 2 cm.

The heating cell consists of two components; one portion of the apparatus slides out entirely to allow for easily manipulation and exchange of the samples (a schematic is shown in Figure 19). The sample is placed within an indentation in the removable section and a small aluminum plate is screwed down over it to allow for improved contact with the metal surface below. A thermocouple is fixed on the bottom of the slide-out component, directly inline with the sample above. Feedback from the thermocouple is sent to an Omega CN2002 Programmable Temperature Controller which cycles two resistive heating rods (inserted parallel to the longest axis of the cell) appropriately in order to equilibrate the temperature of the sample at the desired level. The temperature is stable to within $\pm 2^{\circ}$C with an improved stability as the temperature increases.
As the heating apparatus was being redesigned, we were also trying to determine the best way to achieve cooling capabilities. In order to avoid the inconvenience of having to consistently supply liquid nitrogen, thermoelectric coolers (TECs) were investigated as our method of cooling as opposed to the standard liquid nitrogen cold finger. The solid state TECs (Peltier coolers) have the advantage of being compact and requiring only a power supply to operate. Combinations of several TECS, purchased from Melcor and TE Technology, INC., were used to cool small copper or aluminum plates (less than 18 cubic mm) from room temperature. A thermocouple was mounted on the hot side of the largest TEC and another was mounted on the exposed side of the metal plate to determine the total change in temperature ($\Delta T$). Various heat dissipation methods, (to cool the hot side of the TEC), were also used, including fans, ice water and
dry ice baths, and fluid circulation. However, we were unable to achieve the desired temperature of at least 100 °C below room temperature. Our best result was a ΔT of 98°C, with a cold side temperature of -30°C, and no thermal load using a 3 stage cooler.

TECs are most efficient when cooling a small thermal load, a load much smaller than we were considering for our cooling cell design. In order to accommodate the envisioned thermal load, several TECs would have to be used in parallel, the spatial and power demands of which outweigh the benefits of these coolers for our application. Development of the cooling cell, likely based on a liquid nitrogen cold finger, will be resumed in the future.

4.2.5 Data Collection Methodology

The standard procedure for collecting the Bulk PALS data was to first arrange the sample in the desired configuration and begin the data collection process. In order to have a reduced statistical error, at least one million counts are collected in each spectrum, which, since the coincidence rate was dependent on the set-up used, required varying run times. For example, using sample 59, the coincidence rate in the Normal, Wedge, and Heating configuration were approximately 700, 15 and 400 cps respectively to accumulate at least one million counts the duration of the runs had to be 0.4, 18.5, and 0.7 hours. Wedge mode runs were generally left to accumulate overnight. For the room temperature study, many runs over the course of a few weeks were taken in both the normal and wedge configurations for an improved understanding of the systematic effects.
When a sample was to be heated, a base run was taken at room temperature, as outlined above, in the heating apparatus. The temperature was then raised by either 15 or 20°C and allowed to stabilize before the next data run was started. A complete temperature scan consisted of either heating or cooling the sample in increments of 15 or 20°C between the range of 20 to 160°C. When possible, each complete scan was collected in the same day. A full temperature analysis for a particular sample consisted of an increasing temperature scan to 160°C then allowing the sample to cool to room temperature. The next temperature scan was done by acquiring a spectrum at room temperature and then heating it directly to 160°C. The temperature was then decreased in 15 or 20°C intervals, acquiring spectra at each point. This was the sample was returned to room temperature. Normally a second set of scan were acquired by both heating and then cooling one more.

4.3 Results

4.3.1 Room Temperature Results

A summary for each of the normal and wedge results for the four PTFE samples is presented in Table 3-Table 6. We can see the agreement between the two detector arrangements is reasonable. Differences in crystallinity of the samples are apparent, as with the Beam results, our distinction of 59 and 4602 as high crystallinity samples, and 57 and 147 as low crystallinity samples still holds.
4.3.1. A High Crystallinity Samples

A summary of the results for sample 59 is presented in Table 3. An average $\tau_1$ of 1.31(0.013) ns was measured in the Normal configuration and an average of 1.16(0.03) was found in the Wedge configuration. Both configurations yielded an $I_1$ of approximately 12.0 %. The $\tau_2$ was found to be 4.11 (0.02) ns in Normal configuration and 3.93 (0.02) ns in the Wedge configuration, with an intensity ($I_2$) of $\sim$10%.

Sample 4602 (Table 4), the thicker sample, yielded similar results, except for a surprisingly low $\tau_2$. This sample was run extensively and $\tau_2$ was consistently found to be approximately 3.5 ns, as compared to 4ns as measured in the other samples, this difference was not at all evident in the Beam data. From this we must conclude that the pores in the amorphous region of this sample are smaller than in the other samples.

<table>
<thead>
<tr>
<th>Run Label</th>
<th>Counts (in M)</th>
<th>$\tau_1$ (ns)</th>
<th>$I_1$ (%)</th>
<th>Corrected $I_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$I_2$ (%)</th>
<th>Corrected $I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal - Run 1</td>
<td>7.5</td>
<td>1.403 (0.023)</td>
<td>10.95 (0.18)</td>
<td>13.39</td>
<td>4.218 (0.018)</td>
<td>9.91 (0.13)</td>
<td>12.11</td>
</tr>
<tr>
<td>Normal - Run 2</td>
<td>1.6</td>
<td>1.361 (0.042)</td>
<td>9.77 (0.39)</td>
<td>11.66</td>
<td>4.165 (0.038)</td>
<td>8.33 (0.22)</td>
<td>9.94</td>
</tr>
<tr>
<td>Normal - Run 3</td>
<td>1.6</td>
<td>1.186 (0.068)</td>
<td>10.76 (0.47)</td>
<td>12.34</td>
<td>4.000 (0.065)</td>
<td>8.96 (0.28)</td>
<td>10.27</td>
</tr>
<tr>
<td>Normal - Run 4</td>
<td>1.6</td>
<td>1.510 (0.110)</td>
<td>8.92 (0.43)</td>
<td>11.11</td>
<td>4.200 (0.130)</td>
<td>7.97 (0.50)</td>
<td>9.93</td>
</tr>
<tr>
<td>Normal - Run 5</td>
<td>1.6</td>
<td>1.305 (0.081)</td>
<td>10.43 (0.50)</td>
<td>12.48</td>
<td>4.173 (0.079)</td>
<td>8.42 (0.36)</td>
<td>10.07</td>
</tr>
<tr>
<td>Normal - Run 6</td>
<td>1.6</td>
<td>1.297 (0.082)</td>
<td>10.12 (0.53)</td>
<td>11.96</td>
<td>4.112 (0.089)</td>
<td>8.45 (0.36)</td>
<td>9.99</td>
</tr>
<tr>
<td>Normal - Run 7</td>
<td>1.6</td>
<td>1.290 (0.048)</td>
<td>9.78 (0.39)</td>
<td>11.55</td>
<td>4.054 (0.035)</td>
<td>8.73 (0.21)</td>
<td>10.31</td>
</tr>
<tr>
<td>Normal - Run 8</td>
<td>1.6</td>
<td>1.193 (0.080)</td>
<td>10.20 (0.66)</td>
<td>11.92</td>
<td>3.956 (0.076)</td>
<td>9.15 (0.34)</td>
<td>10.69</td>
</tr>
<tr>
<td>Normal - Run 9</td>
<td>6.9</td>
<td>1.284 (0.038)</td>
<td>10.07 (0.22)</td>
<td>11.82</td>
<td>4.113 (0.038)</td>
<td>8.61 (0.16)</td>
<td>10.10</td>
</tr>
<tr>
<td>Wedge - Run 1</td>
<td>6.4</td>
<td>1.217 (0.037)</td>
<td>12.29 (0.60)</td>
<td></td>
<td>4.049 (0.035)</td>
<td>10.58 (0.44)</td>
<td></td>
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<tr>
<td>Wedge - Run 2</td>
<td>1.6</td>
<td>1.087 (0.045)</td>
<td>13.60 (1.20)</td>
<td></td>
<td>3.958 (0.060)</td>
<td>10.41 (0.86)</td>
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<tr>
<td>Wedge - Run 3</td>
<td>0.3</td>
<td>1.080 (0.130)</td>
<td>13.40 (1.60)</td>
<td></td>
<td>3.920 (0.130)</td>
<td>10.83 (0.66)</td>
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<tr>
<td>Wedge - Run 4</td>
<td>1.6</td>
<td>1.099 (0.050)</td>
<td>12.17 (0.57)</td>
<td></td>
<td>3.835 (0.041)</td>
<td>9.22 (0.22)</td>
<td></td>
</tr>
<tr>
<td>Wedge - Run 5</td>
<td>1.5</td>
<td>1.252 (0.056)</td>
<td>10.08 (0.39)</td>
<td></td>
<td>3.862 (0.046)</td>
<td>8.57 (0.21)</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Sample 4602 room temperature Bulk PALS results

<table>
<thead>
<tr>
<th>Run Label</th>
<th>Counts (in M)</th>
<th>$\tau_1$ (ns)</th>
<th>$I_1$ (%)</th>
<th>Corrected $I_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$I_2$ (%)</th>
<th>Corrected $I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal - 1 - Run 1</td>
<td>2.0</td>
<td>1.377 (0.097)</td>
<td>11.58 (0.41)</td>
<td>14.62</td>
<td>3.730 (0.130)</td>
<td>8.53 (0.63)</td>
<td>10.77</td>
</tr>
<tr>
<td>Normal - 1 - Run 2</td>
<td>3.5</td>
<td>1.387 (0.062)</td>
<td>9.99 (0.27)</td>
<td>12.53</td>
<td>3.670 (0.060)</td>
<td>7.76 (0.32)</td>
<td>9.74</td>
</tr>
<tr>
<td>Normal - 1 - Run 3</td>
<td>2.7</td>
<td>1.026 (0.065)</td>
<td>12.01 (0.82)</td>
<td>14.00</td>
<td>3.401 (0.074)</td>
<td>8.59 (0.35)</td>
<td>10.01</td>
</tr>
<tr>
<td>Normal - 1 - Run 4</td>
<td>9.9</td>
<td>1.234 (0.041)</td>
<td>10.65 (0.18)</td>
<td>12.29</td>
<td>3.580 (0.048)</td>
<td>7.87 (0.21)</td>
<td>9.08</td>
</tr>
<tr>
<td>Normal - 2 - Run 1</td>
<td>11.3</td>
<td>1.027 (0.036)</td>
<td>10.89 (0.42)</td>
<td>12.35</td>
<td>3.348 (0.035)</td>
<td>8.14 (0.17)</td>
<td>9.23</td>
</tr>
<tr>
<td>Normal - 2 - Run 2</td>
<td>178.9</td>
<td>1.245 (0.011)</td>
<td>9.44 (0.05)</td>
<td>11.13</td>
<td>3.543 (0.012)</td>
<td>7.17 (0.05)</td>
<td>8.45</td>
</tr>
<tr>
<td>Normal - 2 - Run 3</td>
<td>59.9</td>
<td>1.225 (0.006)</td>
<td>9.38 (0.02)</td>
<td>11.04</td>
<td>3.499 (0.004)</td>
<td>7.32 (0.02)</td>
<td>8.62</td>
</tr>
<tr>
<td>Wedge - 1 - Run 1</td>
<td>2.0</td>
<td>1.045 (0.054)</td>
<td>14.86 (0.66)</td>
<td>3.472 (0.078)</td>
<td>10.06 (0.37)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - 1 - Run 2</td>
<td>12.5</td>
<td>1.121 (0.026)</td>
<td>13.78 (0.02)</td>
<td>3.499 (0.034)</td>
<td>9.75 (0.16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge-1 &quot;weak&quot;</td>
<td>3.8</td>
<td>1.361 (0.028)</td>
<td>14.30 (0.23)</td>
<td>3.800 (0.028)</td>
<td>9.31 (0.18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - 2 - Run 1</td>
<td>1.6</td>
<td>1.122 (0.084)</td>
<td>14.80 (1.30)</td>
<td>3.544 (0.080)</td>
<td>11.16 (0.82)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - 2 - Run 2</td>
<td>1.1</td>
<td>1.044 (0.061)</td>
<td>15.53 (0.76)</td>
<td>3.437 (0.086)</td>
<td>11.45 (0.46)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - 2 - Run 3</td>
<td>15.7</td>
<td>0.969 (0.018)</td>
<td>13.00 (0.32)</td>
<td>3.266 (0.016)</td>
<td>9.64 (0.10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - 2 - Run 4</td>
<td>3.1</td>
<td>1.201 (0.066)</td>
<td>11.59 (0.38)</td>
<td>3.512 (0.090)</td>
<td>8.28 (0.38)</td>
<td></td>
<td></td>
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<tr>
<td>Wedge - 2 - Run 5</td>
<td>48.9</td>
<td>1.019 (0.015)</td>
<td>12.35 (0.19)</td>
<td>3.333 (0.017)</td>
<td>9.36 (0.08)</td>
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<td></td>
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<tr>
<td>Wedge - 2 - Run 6</td>
<td>9.8</td>
<td>0.987 (0.027)</td>
<td>12.64 (0.36)</td>
<td>3.294 (0.029)</td>
<td>9.48 (0.15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.1.B Low Crystallinity Samples

Sample 57 (Table 5) has an average $\tau_1$ 1.30 (0.03) ns in the normal configuration and of 1.12 (0.02) ns in the wedge configuration. $I_1$ was found to be ~14 %. The $\tau_2$ was found to be 4.27 (0.02) ns and 4.10 (0.02) ns in the Normal and Wedge configuration respectively. $I_2$ was ~15 %, giving 57 a Ps-formation fraction (total Ps intensity) of ~29%. This value is significantly higher than the calculated Ps-formation fraction found in the other samples (~22%). A possible explanation for this difference may be found in the chemical composition of the sample.

Sample 147 yielded slightly lower lifetimes for $\tau_1$ and $\tau_2$ than were found in 57, with average values in the normal configuration of 1.23 (0.02) ns in the crystalline regions and 4.11 (0.01) in the amorphous regions. The lifetime intensities, we also smaller, with $I_1$ measured as ~11% and $I_2$ ~12.5%. It is apparent that this sample and 57 must be different materials.
Table 5. Sample 57 room temperature Bulk PALS results

<table>
<thead>
<tr>
<th>Run Label</th>
<th>Counts (in M)</th>
<th>$\tau_1$ (ns)</th>
<th>$I_1$ (%)</th>
<th>Corrected $I_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$I_2$ (%)</th>
<th>Corrected $I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal - Run 1</td>
<td>3.1</td>
<td>1.227 (0.054)</td>
<td>12.74 (0.45)</td>
<td>15.04</td>
<td>4.296 (0.058)</td>
<td>14.64 (0.33)</td>
<td>17.29</td>
</tr>
<tr>
<td>Normal-Run 2</td>
<td>2.3</td>
<td>1.301 (0.082)</td>
<td>10.76 (0.45)</td>
<td>13.19</td>
<td>4.426 (0.086)</td>
<td>12.49 (0.43)</td>
<td>15.31</td>
</tr>
<tr>
<td>Normal-Run 3</td>
<td>3.3</td>
<td>1.429 (0.092)</td>
<td>8.99 (0.36)</td>
<td>12.02</td>
<td>4.271 (0.072)</td>
<td>11.33 (0.39)</td>
<td>15.15</td>
</tr>
<tr>
<td>Normal-Run 4</td>
<td>13.5</td>
<td>1.260 (0.032)</td>
<td>11.16 (0.21)</td>
<td>12.97</td>
<td>4.182 (0.029)</td>
<td>12.34 (0.17)</td>
<td>14.34</td>
</tr>
<tr>
<td>Norm-&quot;weak&quot; source</td>
<td>2.5</td>
<td>1.280 (0.049)</td>
<td>11.93 (0.46)</td>
<td>13.74</td>
<td>4.339 (0.053)</td>
<td>11.71 (0.38)</td>
<td>13.49</td>
</tr>
<tr>
<td>Wedge - Run 1</td>
<td>2.5</td>
<td>1.118 (0.035)</td>
<td>14.92 (0.52)</td>
<td>4.117 (0.027)</td>
<td>14.83 (0.24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - Run 2</td>
<td>11.1</td>
<td>1.127 (0.025)</td>
<td>14.44 (0.31)</td>
<td>4.116 (0.023)</td>
<td>15.62 (0.18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge- Run 3</td>
<td>9.8</td>
<td>1.105 (0.022)</td>
<td>14.30 (0.30)</td>
<td>4.087 (0.014)</td>
<td>15.47 (0.13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Sample 147 room temperature Bulk PALS results

<table>
<thead>
<tr>
<th>Run Label</th>
<th>Counts (in M)</th>
<th>$\tau_1$ (ns)</th>
<th>$I_1$ (%)</th>
<th>Corrected $I_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$I_2$ (%)</th>
<th>Corrected $I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal - Run 1</td>
<td>5.5</td>
<td>1.362 (0.075)</td>
<td>7.91 (0.25)</td>
<td><strong>9.39</strong></td>
<td>4.203 (0.057)</td>
<td>9.94 (0.03)</td>
<td><strong>11.80</strong></td>
</tr>
<tr>
<td>Normal - Run 2</td>
<td>8.7</td>
<td>1.233 (0.049)</td>
<td>8.63 (0.28)</td>
<td><strong>9.89</strong></td>
<td>4.115 (0.042)</td>
<td>10.28 (0.17)</td>
<td><strong>11.78</strong></td>
</tr>
<tr>
<td>Normal - Run 3</td>
<td>6.7</td>
<td>1.273 (0.059)</td>
<td>8.40 (0.27)</td>
<td><strong>9.78</strong></td>
<td>4.141 (0.045)</td>
<td>10.14 (0.20)</td>
<td><strong>11.79</strong></td>
</tr>
<tr>
<td>Normal - Run 4</td>
<td>6.7</td>
<td>1.208 (0.052)</td>
<td>8.96 (0.33)</td>
<td><strong>10.24</strong></td>
<td>4.083 (0.043)</td>
<td>10.27 (0.19)</td>
<td><strong>11.73</strong></td>
</tr>
<tr>
<td>Normal - Run 5</td>
<td>4.3</td>
<td>1.066 (0.051)</td>
<td>9.87 (0.60)</td>
<td><strong>11.12</strong></td>
<td>4.004 (0.031)</td>
<td>10.72 (0.18)</td>
<td><strong>12.08</strong></td>
</tr>
<tr>
<td>Normal - Run 6</td>
<td>175.3</td>
<td>1.219 (0.011)</td>
<td>8.63 (0.07)</td>
<td><strong>9.96</strong></td>
<td>4.10 (0.008)</td>
<td>10.26 (0.04)</td>
<td><strong>11.84</strong></td>
</tr>
<tr>
<td>Normal - Run 7</td>
<td>263.4</td>
<td>1.234 (0.009)</td>
<td>8.57 (0.06)</td>
<td><strong>9.92</strong></td>
<td>4.117 (0.008)</td>
<td>10.13 (0.03)</td>
<td><strong>11.74</strong></td>
</tr>
<tr>
<td>Wedge - Run 1</td>
<td>1.9</td>
<td>1.045 (0.072)</td>
<td>12.30 (0.94)</td>
<td>4.095 (0.054)</td>
<td>13.04 (0.31)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - Run 2</td>
<td>10.7</td>
<td>1.082 (0.036)</td>
<td>11.04 (0.38)</td>
<td>3.998 (0.026)</td>
<td>13.01 (0.15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wedge - Run 3</td>
<td>27.9</td>
<td>1.030 (0.021)</td>
<td>11.47 (0.32)</td>
<td>3.968 (0.015)</td>
<td>12.77 (0.10)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In conclusion, while from the Beam results might lead one to believe that the crystallinity pairs (59 with 4602 and 147 with 57) were the same material, but with different thickness, the room temperature Bulk results indicate otherwise. The smaller amorphous pore size in 4602 distinguishes this sample from 59, thought formerly to be its thinner high crystallinity counterpart. The higher Ps-formation fraction of sample 57 distinguishes it from the thinner 147.
4.3.2 Heating Results

Figure 20-Figure 27 show the dependence of the amorphous and crystalline pore sizes, and their intensities, on temperature. Generally $\tau_1$ and $I_1$ are independent of, or have only a slight dependence on temperature. However, $\tau_2$ and $I_2$ exhibit a strong dependence on temperature. We assume this dependence is roughly linear for $I_2$. Several data points were largely out of agreement with our suggested dependence, likely due to the volatility of fitting the two Ps lifetimes. $I_2$ was adjusted to fit the linear function and then fixed to this value, for select points with each sample. The fat pink arrows on the $I_2$ plots are drawn from the original value to the new, fixed value. The new $\tau_2$ lifetimes for the points with a fixed $I_2$ were noted and the plots adjusted appropriately. Generally a decrease in the intensity resulted in an increase in the corresponding lifetime, likewise an increase in the intensity resulted in a decreased lifetime. The trend of $\tau_2$ in response to temperature is shown as a black line in the respective plots. One should note that fixing $I_2$ will also affect the values of $I_1$ and $\tau_1$; however the figures below show the initial values.

4.3.2. A High Crystallinity samples

Figure 20 and Figure 21 show the heating results for sample 59, the thin, high crystallinity film. $\tau_1$ and $I_1$ exhibit no temperature dependence. $\tau_2$ increases from $\sim 4.2\%$ to $\sim 5.0\%$ over the temperature range yielding a $d\tau_2/dT$ of $0.0057 \text{ ns}/^\circ\text{C}$. $I_1$ also increases with temperature, from $\sim 7.5\%$ to $\sim 12\%$ over the temperature range.

The thick, high crystallinity sample, 4602 (Figure 22 and Figure 23), showed a similar response to temperature. While, there is a slight hint of an increase in $\tau_1$ and
decrease in $I_1$, given the correlation between $\tau_1$ and $I_1$ these may actually be temperature independent. $\tau_2$ in 4602 showed a slightly more temperature dependence than it had in sample 59, increasing from ~3.3% to ~4.35% over the temperature range for a $d\tau_2/dT$ of 0.0077 ns/°C. The increase in $I_1$ was increases from ~7% to ~11% over the temperature range, which is comparable to the change observed in 59.

4.3.2.B Low Crystallinity Samples

Sample 147, the thin, low crystallinity film showed results comparable to those found in the high crystallinity samples (Figure 26 and Figure 27). $\tau_1$ and $I_1$ are reasonably temperature independent and $I_2$ shows the standard increase from ~7.0% to ~12% over the temperature range. $\tau_2$ increases from ~4.0% to ~5.0% over the temperature range with a $d\tau_2/dT$ of 0.0083 ns/°C.

The thick, low crystallinity sample, 57, was the only film to produce unique results (Figure 24 and Figure 25). Once again, there is a slight hint of an increase in $\tau_1$ and decrease in $I_1$, but as mentioned for sample 4602, given the correlation between $\tau_1$ and $I_1$ these may actually be temperature independent. $\tau_2$ shows a typical increases from ~4.2% to ~5.2% over the temperature range with a $d\tau_2/dT$ of 0.0074 ns/°C. However, unlike in the previous films, $I_2$ remains constant over the temperature range.
Figure 20. Sample 59 heating results for $\tau_1$ and $I_1$
Figure 21. Sample 59 heating results for $\tau_2$ and $I_2$. 
Figure 22. Sample 4602 heating results for $\tau_1$ and $I_1$.
Figure 23. Sample 4602 heating results for $\tau_2$ and $I_2$. 
Figure 24. Sample 57 heating results for $\tau_1$ and $I_1$.
Figure 25. Sample 57 heating results for $\tau_2$ and $I_2$.
Figure 26. Sample 147 heating results for $\tau_1$ and $I_1$. 
Figure 27. Sample 147 heating results for $\tau_2$ and $I_2$. 

The graph shows the relationship between temperature and $\tau_2$ and $I_2$. The data is divided into five runs: Run 1 (increasing T), Run 2 (decreasing T), Run 2.5 (decreasing T), Run 3 (increasing T), and Run 4 (decreasing T). The temperature is plotted on the x-axis in degrees Celsius, while $\tau_2$ (in ns) and $I_2$ (%) are plotted on the y-axes. The error bars indicate the variability in the measurements. The trend lines suggest a positive correlation between temperature and both $\tau_2$ and $I_2$. 

The data points for each run are color-coded to differentiate between them. The runs appear to follow different patterns, with Run 1 and Run 4 showing a clear increase in both $\tau_2$ and $I_2$ with increasing temperature, while Run 2 and Run 3 show a decrease.
5. Conclusions

5.1 Comparison of Bulk and Beam Results

Our study of semi-crystalline PTFE using Beam and Bulk PALS has proven to be very effective at characterizing the porosity of the material and correlating it with film permeability. The Beam apparatus was able to provide us with a good picture of the surface structure of the samples. Sample 59 exhibited evidence of a front-to-back difference in surface crystallinity, which may have been caused by a difference in the temperature of the two sides as the material crystallized. The PALS analysis provided strong evidence for a surface contamination on sample 4602-2, and perhaps lesser contamination of 4602-1 and the 147 samples. The Beam results showed a clear difference between the crystallinity of the samples where samples 4602 and 59 have high crystallinity and 147 and 57 exhibited a lower crystallinity. The Ps lifetimes in both the crystalline and amorphous domains are consistent across the samples. The results from this portion led to the belief that perhaps the four samples were just two different materials, each with a thick and thin film.

The Bulk PALS technique allowed us to further distinguish the samples; a summary of the room temperature Bulk PALS results for the four samples is presented in Table 7. The short lifetime, $\tau_1$, constant in all four samples, corresponds to a spherical pore diameter of approximately 4.0 Å. The longer lifetime, $\tau_2$, is similar for samples 59, 57, and 147 and corresponds to a pore diameter of $\sim$8.5 Å. Sample 4602 exhibited a consistently lower $\tau_2$, with a diameter closer to 7.8 Å. Therefore the pores in the
amorphous region of 4602 are *smaller* than in the other samples. This phenomenon was not apparent in the Beam data, so we must either conclude that these smaller pores are in the bulk, but not the surface of the 4602 samples, or that backscattering in the Beam apparatus “washed out” this effect. The supplier did confirm that 4602 was the one film they did not make; hence the lower \( \tau_2 \) is quite possibly due to the difference in fabrication procedures.

Differences in the crystallinity were also apparent for these films, confirming the Beam results. Looking at the relative (fractional) intensity of the crystalline regions (the last column of Table 7), one can see that these films group into two distinct classes of 59 and 4602 as high crystallinity samples \( (I_1/(I_1+I_2) > 0.5) \), and 57 and 147 as low crystallinity samples \( (I_1/(I_1+I_2) < 0.5) \). Sample 57 was found to have a higher Ps-formation fraction (total Ps intensity) than the other samples, a higher Ps intensity may result from differences in the chemical composition of the sample, or may be an indication that sample 57 is more porous than the other films.

**Table 7.** Average values from Table 3-Table 6. Typical error in the last column is ±0.008. A high value in the last column indicates higher crystallinity. Important values are in bold.

<table>
<thead>
<tr>
<th>Run Label</th>
<th>( \tau_1 ) (ns)</th>
<th>( I_1 ) (%)</th>
<th>( \tau_2 ) (ns)</th>
<th>( I_2 ) (%)</th>
<th>( I_1 + I_2 ) (%)</th>
<th>( I_1/(I_1+I_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>59 normal</td>
<td>1.31 (0.013)</td>
<td>12.0 (0.2)</td>
<td>4.11 (0.02)</td>
<td>10.4 (0.1)</td>
<td>22.4</td>
<td>0.536</td>
</tr>
<tr>
<td>59 wedge</td>
<td>1.16 (0.03)</td>
<td>12.0 (0.25)</td>
<td>3.93 (0.02)</td>
<td>9.7 (0.2)</td>
<td>21.7</td>
<td>0.553</td>
</tr>
<tr>
<td>4602 normal</td>
<td>1.22 (0.02)</td>
<td>12.6 (0.1)</td>
<td>3.54 (0.01)</td>
<td>9.4 (0.1)</td>
<td>22.0</td>
<td>0.573</td>
</tr>
<tr>
<td>4602 wedge</td>
<td>1.10 (0.02)</td>
<td>13.7 (0.2)</td>
<td>3.45 (0.02)</td>
<td>9.8 (0.1)</td>
<td>23.5</td>
<td>0.583</td>
</tr>
<tr>
<td>57 normal</td>
<td>1.30 (0.03)</td>
<td>13.4 (0.2)</td>
<td>4.27 (0.02)</td>
<td>15.1 (0.2)</td>
<td>28.5</td>
<td>0.470</td>
</tr>
<tr>
<td>57 wedge</td>
<td>1.12 (0.02)</td>
<td>14.5 (0.2)</td>
<td>4.10 (0.02)</td>
<td>15.5 (0.12)</td>
<td>30.0</td>
<td>0.483</td>
</tr>
<tr>
<td>147 normal</td>
<td>1.23 (0.02)</td>
<td>10.1 (0.15)</td>
<td>4.11 (0.01)</td>
<td>11.8 (0.1)</td>
<td>21.9</td>
<td>0.461</td>
</tr>
<tr>
<td>147 wedge</td>
<td>1.05 (0.02)</td>
<td>11.6 (0.3)</td>
<td>4.02 (0.02)</td>
<td>12.9 (0.1)</td>
<td>24.5</td>
<td>0.473</td>
</tr>
</tbody>
</table>
The heating of these four films did not provide any unexpected results. The lack of temperature dependence of $I_2$ for sample 57 was the only unique feature of this series of measurements. As anticipated the amorphous, but not the crystalline regions of the polymer exhibited a significant dependence on temperature. We did not find, nor did we expect to find any transition temperatures in the range scanned (recall Dlubek et al found $T_g = 195$ K [6]). The results from the heating data can be found in Table 8, which summarizes the data collected for this thesis.

Table 8. Average values for several of the variables explored in this thesis ordered from what we believe to be the least permeable sample to the most permeable

<table>
<thead>
<tr>
<th>ID</th>
<th>Permeable?</th>
<th>$\tau_2 \pm 0.04$ ns</th>
<th>$d\tau_2/dT \pm 0.15$ ns/$^\circ$C</th>
<th>$I_2 \pm 0.15%$</th>
<th>$I_1+I_2 \pm 0.2%$</th>
<th>$I_1/(I_1+I_2) \pm 0.010$</th>
<th>$I_2 \pm 0.15%$</th>
<th>$I_1/(I_1+I_2) \pm 0.010$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4602</td>
<td>Least</td>
<td>3.50 ns</td>
<td>0.0077</td>
<td>9.6%</td>
<td>22.7%</td>
<td>0.578</td>
<td>7.0%</td>
<td>0.640</td>
</tr>
<tr>
<td>59</td>
<td></td>
<td>4.02 ns</td>
<td>0.0057</td>
<td>10.0%</td>
<td>22.0%</td>
<td>0.545</td>
<td>7.5%</td>
<td>0.604</td>
</tr>
<tr>
<td>147</td>
<td></td>
<td>4.06 ns</td>
<td>0.0083</td>
<td>12.3%</td>
<td>23.0%</td>
<td>0.467</td>
<td>9.0%</td>
<td>0.547</td>
</tr>
<tr>
<td>57</td>
<td>Highest</td>
<td>4.18 ns</td>
<td>0.0074</td>
<td>15.3%</td>
<td>29.2%</td>
<td>0.476</td>
<td>9.5%</td>
<td>0.527</td>
</tr>
</tbody>
</table>

Table 8 summarizes the PALS results for this thesis, the samples are ordered with respect to the samples measured permeability (provided by the supplier). The Bulk PALS data are consistent with this trend in permeability. We expect that as the porosity of the film increases, due to increased pore size in the amorphous region or increased density (concentration) of the pores in the amorphous region, the films permeability will be higher. These results clearly show that permeability increases with the size of the
amorphous pores, and decreases with increasing crystallinity. The 4602 film with the largest crystallinity parameter of $I_1/I_{TOT} = 0.640$ and a smaller amorphous pore lifetime of 3.5 ns has the lowest permeability. Conversely the 57 film, with the lowest crystallinity factor of 0.527 and the highest Ps intensity has the largest permeability. PALS is clearly able to distinguish these films and provide a strong correlation to permeability.

5.2 Further Applications

As demonstrated with the PALS results, we are clearly able to correlate porosity with permeability. PALS therefore has the potential to be a vigorous method for characterization of permeable and semi-permeable materials. Permeability related information is useful to companies involved in semi-permeable membrane technologies such as PEM fuel cells.

To this end, our current work includes the analysis of permeable Nafion® polymer used in PEM fuel cells. The samples, provided by Giner, INC, are being analyzed using the Bulk system in a humidity environment (fuel cells are naturally wet), and in the future will be dried for comparison. They have also been analyzed dry in the Beam system. This work will increase our experience characterizing semi-permeable materials and allow us to investigate possible differences in the behavior of Ps in moist environments. The work also serves to continue or investigation of the correlations between the free volume characterization of semi-crystalline materials and film porosity.
A. Atomic Lifetime Fitting

The lifetime fitting techniques used in this thesis are applicable outside of PALS experiments. Last year I became involved in the analysis of atomic lifetime data collected by Professor Chris Monroe’s group for precision lifetime measurements of excited state lifetimes of a single trapped Cd$^+$ ion. Systematic effects due to an asymmetric and broad time resolution function convolved with “prompt events” made it complicated to extract the excited state lifetimes from the data. Two different excited states of ~2.6 and ~3.1 ns were studied. My involvement in the data analysis (to be outlined below) provided lifetime fitting experience relevant to this thesis.

Using POSFIT, I fit the prepared spectrum to a single exponential lifetime and a fixed background (determined by examining the spectrum) over a time range $\Delta t = t_{\text{stop}} - t_{\text{start}}$. The stop time of the fit, $t_{\text{stop}}$, was fixed, typically to 8 ns (80 channels) from the peak and the start time was increased by 1 channel (0.1 ns) increments out to 6.0 ns from the peak (refer to Figure 2(b) of the paper for an illustration of the data used). A simple program I wrote was then used to quickly reformat the results from POSFIT so that they could easily be imported into Excel. I then plotted these fitted lifetimes versus the start time of the fit (see the black points on Figure 28).

Next, I used a Matlab program written by M.J. Madsen to generate a spectrum in which a pure exponential (meant to represent the actual transition lifetime $\tau$) and a prompt peak (modeled as a delta function in channel 1 of the exponential) is convolved with the measured resolution function. A prompt peak multiplier (PPM) was calculated by convolving a pure exponential with the approximate true lifetime, intensity $I_p$, and then subtracting that from the real data for a difference intensity $I_{\text{diff}}$. The excess events
are integrated and converted into the PPM; PPM = I_{diff} / I_{P}^*(\tau/10). I then fit these generated spectra in the same manner as the real data, as outlined in the above paragraph (see the red, blue, and green points on Figure 28 for an example). I then varied \( \tau \) and plotted the fits with the real data; these plots were used to determine the experimental \( \tau \).

![Figure 28](image-url)  

**Figure 28.** An example of a plot generated in order to fit the atomic lifetime (for the 5p\(^2\)P\(_{3/2}\) transition as measured in the quadrupole trap). For this plot 80 channels of data and a PPM of 2 were used.
Precision lifetime measurements of a single trapped ion with ultrafast laser pulses


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We report precision measurements of the excited state lifetime of the $5p \ 2^3P_{1/2}$ and $5p \ 2^3P_{3/2}$ levels of a single trapped Cs$^+$ ion. Combining ion trap and ultrafast laser technologies, the ion is excited with picosecond laser pulses from a mode-locked laser and the distribution of arrival times of spontaneously emitted photons is recorded. The resulting lifetimes are $3.148\pm0.011$ ns and $2.647\pm0.010$ ns for $2^3P_{1/2}$ and $2^3P_{3/2}$ respectively. With a total uncertainty of under 0.4%, these are among the most precise measurements of any atomic state lifetimes to date.

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PACS numbers: 32.80.Pj, 32.70.Cs, 42.50.Vk

Precise measurements of atomic data are of great interest throughout many fields of science. Lifetime measurements are of particular importance to the interpretation of measurements of atomic parity nonconservation [1], tests of QED and atomic structure theory [2], and even astrophysical applications [3]. Because of this, there is a need for more accurate ways of measuring excited state lifetimes. Previous methods include time-correlated single photon techniques [4–9], beam-foil experiments [5], fast beam measurements [10,11], electron-photon decay coincidence techniques [12,13], luminescent decay [14,15], linewidth measurements [16], photoassociative spectroscopy [17], and quantum jump methods [18].

Here we report exact state lifetime measurements using a time-correlated single photon-counting technique. The experiment uniquely combines the isolation of single laser-cooled trapped ions with the precise timing of ultrafast lasers. This method, designed especially to eliminate common systematic errors, involves selective excitation of a single trapped ion to a particular excited state (lifetime of order nanoseconds) by an ultrafast laser pulse (duration of order picoseconds). Arrival of the spontaneously emitted photon from the ion is correlated in time with the excitation pulse, and the excited state lifetime is extracted from the distribution of time delays from such events.

By performing the experiment on a single trapped ion [6,7,18], we are able to eliminate prevalent systematic errors, such as pulse pileup that causes multiple photons to be collected within the time resolution of the detector, radiation trapping or the absorption and re-emission of radiation by neighboring atoms, atoms disappearing from view before decaying, and substrate or superradiance arising from coherent interactions with nearby atoms. By using ultrafast laser pulses [4], we can eliminate potential effects from applied light during the measurement interval including ac Stark shifts, background laser light, and multiphoton excitations which can also lead to pulse pileup.

With this setup, at most one photon can be emitted following an excitation pulse. While this feature is instrumental in eliminating the above systematic errors, it would appear that this signal would require large integration times for reasonable statistical uncertainties. However, with a lifetime of only a few nanoseconds, millions of such excitation can be performed each second, thus potentially allowing sufficient data for a statistical error of under 0.1% to be collected in a matter of minutes [6].

A diagram of the experimental apparatus is shown in Fig. 1. Individual cadmium ions are trapped and isolated in one of two rf quadrupole traps. First, the experiment is conducted using an asymmetric quadrupole trap of characteristic size ~0.7 mm [19] [Fig. 1(c)]. The entire experiment is then repeated in a linear trap with rod spacings of 0.5 mm and an endcap spacing of 2.6 mm [Fig. 1(d)]. Both traps have secular trapping frequencies on the order of $\omega_{0}/2\pi=0.1–1.0$ MHz.

Two types of laser radiation are incident on the ion: pulsed and continuous wave (cw) lasers. The pulsed light is from a picosecond mode-locked Ti:sapphire laser whose center frequency is resonantly tuned to provide excitation to one of the $2P$ states [Fig. 1(b)]. For excitation to the $5p \ 2^3P_{1/2}$ ($5p \ 2^3P_{3/2}$) state, each pulse is frequency quadrupled from 906 to 226.5 nm (858 to 214.5 nm) through phase-matched LBO and BBO nonlinear crystals. The UV is filtered from the fundamental and second harmonic via dichroic mirrors and directed to the ion with a near transform-limited pulse width of $\tau_{\text{p}}=1$ ps. Since the pulsed laser bandwidth (~0.40 THz) is much smaller than the line-structure splitting (~74 THz), selective excitation to the different $2P$ excited states is possible. Each pulse has $E=10$ kJ of energy, which will excite the ion with a probability of approximately 10% [20]: $P_{\text{exc}}=\sin^{2}(\gamma/4\Delta

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FIG. 1. The experimental apparatus. (a) A picosecond mode-locked Ti:sapphire laser is tuned to four times the resonant wavelength for either the 5p 2P 3/2 or the 5p 2P 1/2 level of Cd* each pulse is then frequency-quadrupled through nonlinear crystals, filtered from the fundamental and second harmonics, and directed to the ion. An amplified cw diode laser is also frequency quadrupled and tuned just red of the 2P 3/2 transition for Doppler cooling of the ion within the trap. Acousto-optic modulators (AOMs) are used to switch on and off the lasers as described in the text. Photons emitted from the ion are collected by an f/2.1 imaging lens and directed toward a photon-counting photomultiplier tube (PMT). The output of the PMT provides the start pulse for the time to digital converter (TDC), whereas the stop pulse is provided by the reference clock of the mode-locked laser. (b) The relevant energy levels of Cd*. (c) An asymmetric quadrupole trap. (d) A linear trap.

Following excitation from the pulsed laser, the spontaneously emitted photons are collected by an f/2.1 imaging lens and directed toward a photon-counting photomultiplier tube (PMT) [22]. The output signal of the PMT provides the start pulse for the time-to-digital converter (TDC), whereas the stop pulse is synchronized to the reference clock of the mode-locked laser. This time-reversed mode is used to eliminate dead time in the TDC. The PMT used is a Hamamatsu H16240 Series PMT of quantum efficiency $\approx 20\%$, and the TDC is an ORTEC model 9353 time digitizer that has 100 ps digital time resolution with no interpolator, accuracy within 20 ppm, less than 145 ps time jitter, and an integral nonlinearity within 20 ps rms.

In the experiment, an acousto-optic modulator (AOM) is used to switch on the cw beam to Doppler cool the ion for 500 ns. Following the cooling pulse, a reference clock from the pulsed laser (synchronized with the laser pulse train) triggers an AOM in the pulsed laser beam and directs a number of pulses to the ion ($\approx 15$ pulses, with adjacent pulses separated by $\approx 12.4$ ns). The repetition rate of this cycle is limited to 1 MHz due to the update time of the pulse generator, and during a given excitation pulse the success probability of detecting an emitted photon is $\approx 2 \times 10^{-4}$. This gives an average count rate of about 3000 counts per second and thus an expected statistical precision of $\Delta \tau_{\text{stat}} / \tau = 0.25\% / \sqrt{T}$, where $\tau$ is the excited state lifetime and $T$ is the data collection time in minutes.

Despite the absence of previously mentioned common systematic effects, possible effects that still must be considered in this system include Zeeman and hyperfine quantum beats [31]. Zeeman quantum beats have no significant effect (shifts of $<0.05\%$) when working in sufficiently low magnetic fields ($<0.5$ G), whereas the hyperfine beating is eliminated by using an even isotope of Cd that has no hyperfine structure (i.e., $^{110}$Cd$^*$. Potential effects from off-resonant laser light—ac Stark shifts, background counts, etc.—are also greatly reduced or eliminated in this experiment by taking data only when the cw cooling beam is switched off via the AOM. Hence, immediately following the excitation pulse, the only light present is the single spontaneously emitted photon from the ion. Other possible effects such as relativistic shifts or isotopic dependencies are negligible. Because
TABLE I. Lifetime measurement results (ns). The asymmetric quadrupole and linear trap results are in good statistical agreement for the $2^P_{1/2}$ transition and the final result is a weighted average of the two values (the systematic error is common to both). For the $2^P_{3/2}$ transition, the contribution from the linear trap is omitted from the final result due to an order of magnitude larger prompt peak giving rise to an unusually large systematic error.

<table>
<thead>
<tr>
<th>Trap</th>
<th>Error</th>
<th>$5p^2P_{1/2}$</th>
<th>$5p^2P_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole</td>
<td>...</td>
<td>3.148</td>
<td>2.646</td>
</tr>
<tr>
<td></td>
<td>Statistical</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Systematic</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Linear</td>
<td>...</td>
<td>3.132</td>
<td>2.649</td>
</tr>
<tr>
<td></td>
<td>Statistical</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Systematic</td>
<td>0.000</td>
<td>0.010</td>
</tr>
<tr>
<td>Final results</td>
<td></td>
<td>3.148±0.011</td>
<td>2.647±0.010</td>
</tr>
</tbody>
</table>

this technique is devoid of these typical systematic effects, the only significant errors are those arising from the particular equipment used, as discussed below.

To determine the excited state lifetime, the data in a 12.4 ns range for each laser pulse are summed and time-inverted. These spectra are corrected for uncorrelated background events and then fit to a single exponential lifetime $\tau$. As the start time of the fit is stepped out from the peak $[32]$, the fitted lifetime for the experimental data has an expected systematic bias of 3–5% (a natural consequence of the convolution of the timing system response function [Fig. 2(a)] with the pure exponential decay of the excited state). This effect can be further exacerbated by the presence of “prompt” events from background laser light from the ultrafast excitation pulse that is scattered from the apparatus, described by an additional convolution of a $\delta$ function at $r=0$. The relative intensity of the prompt peak varies between the four measurements, and depends upon the particular optical alignment in each experimental run. The time-response function distorts the spectrum from a pure exponential and has the net effect of shifting events to longer times thereby increasing the fitted lifetime by 3–5%. To account for these time-dependent shifts and extract the true lifetime, a simulated spectrum is generated by convolving the measured time-response function with an exponential decay and $\delta$ function at $r=0$. The relative intensity of the prompt $\delta$ function is straightforwardly determined by subtracting a convolved pure exponential, appropriately normalized in the exponential part of the spectrum, and integrating the remaining events around $r=0$.

The simulated spectra and the real data are fit in precisely the same manner: the start channel of the fit is successively stepped out from $t_1=1$ ns to $t_1=6$ ns. The parameter $\tau$ in the simulated spectra is varied to best match the fitted data over the entire time range. The systematic error in the lifetime is determined by varying $\tau$ until the data over the time range is no longer in statistical agreement with the simulated spectra. While the resulting variation of the fits over the full fitting range for the simulations are sensitive to the choice of the prompt $\delta$-function intensity, the fitted lifetime over the range $t_1=1.7–1.8$ ns is virtually independent of the prompt $\delta$-function intensity and thus the results for the lifetimes and the statistical error bar quoted in Table I are taken from this range of $t_1$. Doing so greatly reduces the systematic uncertainty from the prompt $\delta$-function in all but one set of runs. The presence of an order-of-magnitude larger prompt peak for the $2^P_{1/2}$ transition measured in the linear trap, due to poor optical alignment, results in a significantly larger variation in the fit over the time range and hence the resulting systematic uncertainty for this data set is three times larger than for the other three measurements. Despite this problem, the agreement between the measured $2^P_{3/2}$ lifetimes in both trap apparatuses is nominal, giving us great confidence in our

![Fig. 3. Published results of theoretical (open circles) and experimental (filled circles) lifetimes, including this work (filled diamonds), for the $5p^2P_{1/2}$ and $5p^2P_{3/2}$ states of Cl$^7$.](image-url)
technique to account for the much smaller effects of the prompt scattered events in the other three data sets.

The final values, summarized in Table I for each trap, are 3.148 ± 0.011 ns for the \(^2P_{1/2}\) state and 2.647 ± 0.001 ns for the \(^2P_{3/2}\) state. The final error is the average of the statistical error (less than 0.15\% for all measurements) and the systematic error. The systematic error of approximately 0.4\% is due to the uncertainty in comparison of the fitted values of the convolved spectrum and the experimental data. These new results are plotted in Fig. 3 along with previously reported theoretical and experimental values for these levels. It is seen that the results reported in this paper are the most precise measurements of these particular excited states of Cd\(^{110}\).

In conclusion, to our knowledge, we have demonstrated a new technique for measuring excited state atomic lifetimes that is able to eliminate common systematic errors associated with such measurements. The results herein are not only the most precise to date for Cd\(^{110}\), but with absolute uncertainties of order 10 ps, are among the most precisely measured excited state lifetimes in any atomic system. Furthermore, this technique has the potential to achieve ~100 ppm precision by eliminating the remaining systematic effects due to prompt events and electronic noise. Other possible improvements include increasing the data collection rate by using a faster pulse generator and TDC, measuring a longer decay range by pulse-picking individual pulses.

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[20] It would be possible to increase the data rate by increasing this excitation probability, however, it was kept to near 10\% since higher pulsed laser powers also tend to load extra ions into the trap.
[22] Due to the chromatic aberration of this imaging system, the state-selective light collection between \(^2P_{1/2}\) and \(^2P_{3/2}\) is also achieved.
6. References


