

# Measurements of Fluorescent Properties with an Optical Cryostat

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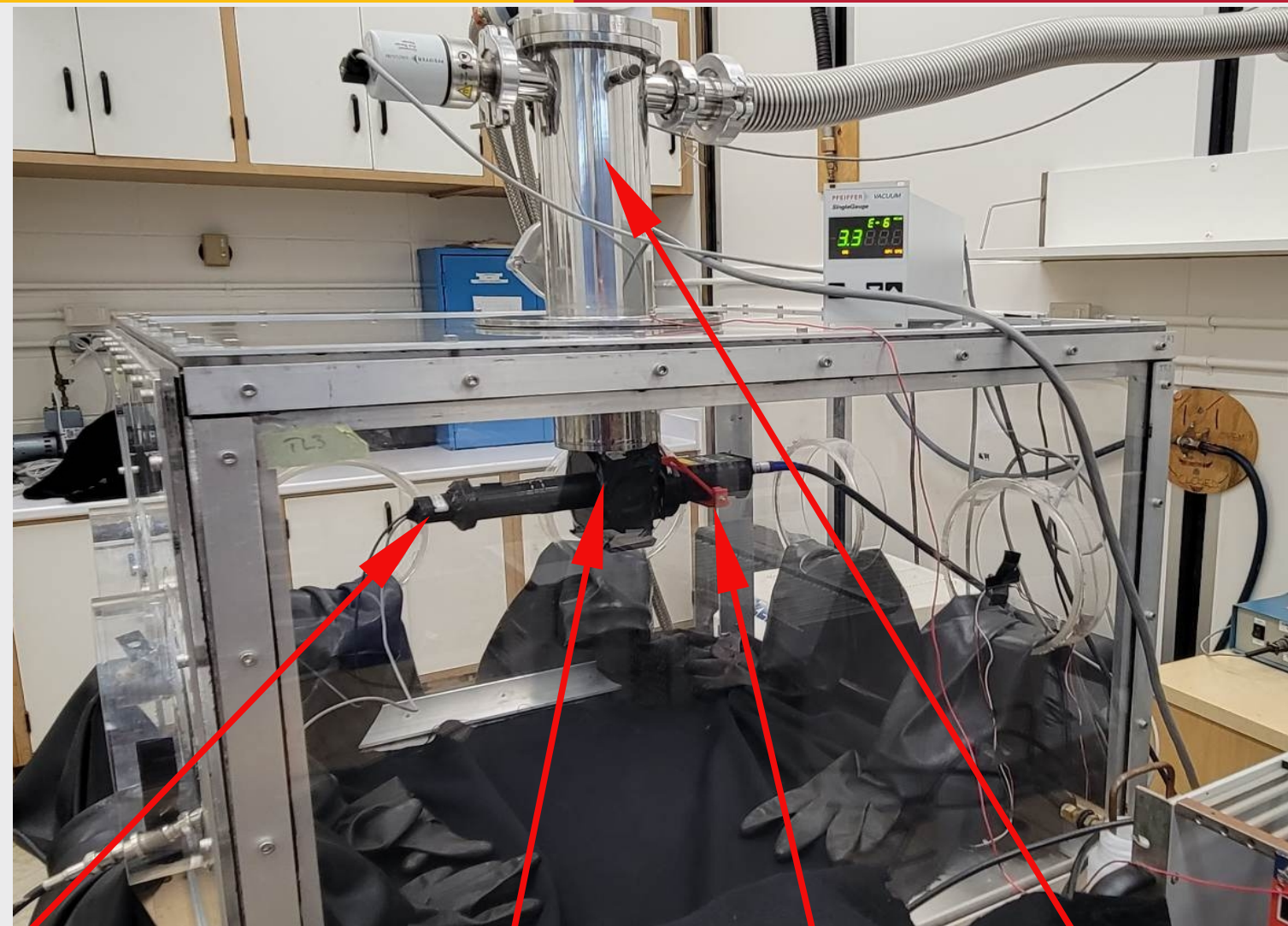


## The Optical Cryostat

The optical cryostat at Queen's attempts to replicate the conditions of a cryogenic rare event detector with cooling capabilities down to 4K.

The cryostat is highly versatile, allowing for customization of the set-up dependent on the requirements of a particular experiment.

Possible measurements include time-resolved fluorescent studies, scintillation experiments, and spectroscopy measurements.



Visible light sensitive PMT

Vacuum shroud (sample contained inside)

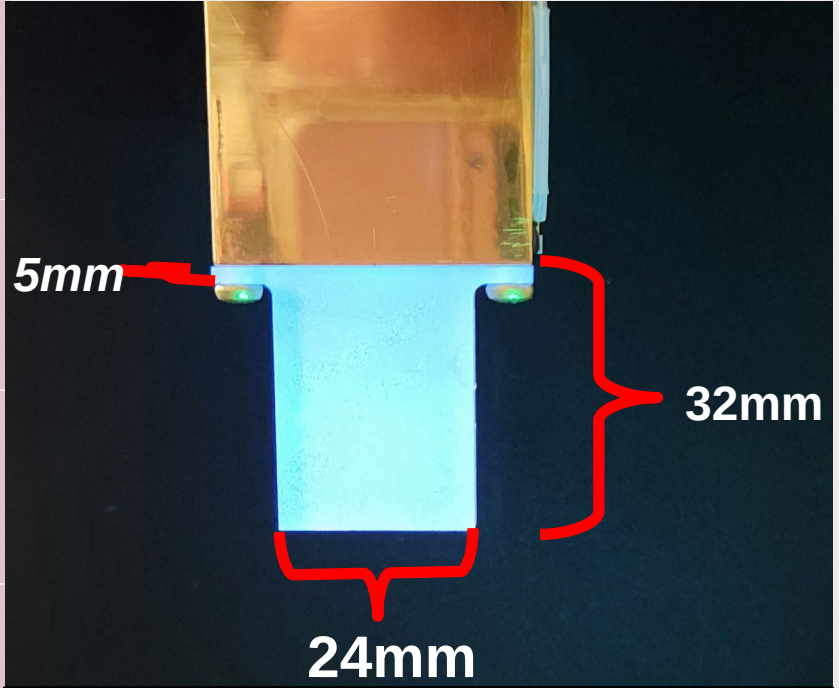
Pulsed UV LED

Cryogenic cooler



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### 3 Previous and Current Sample Measurements

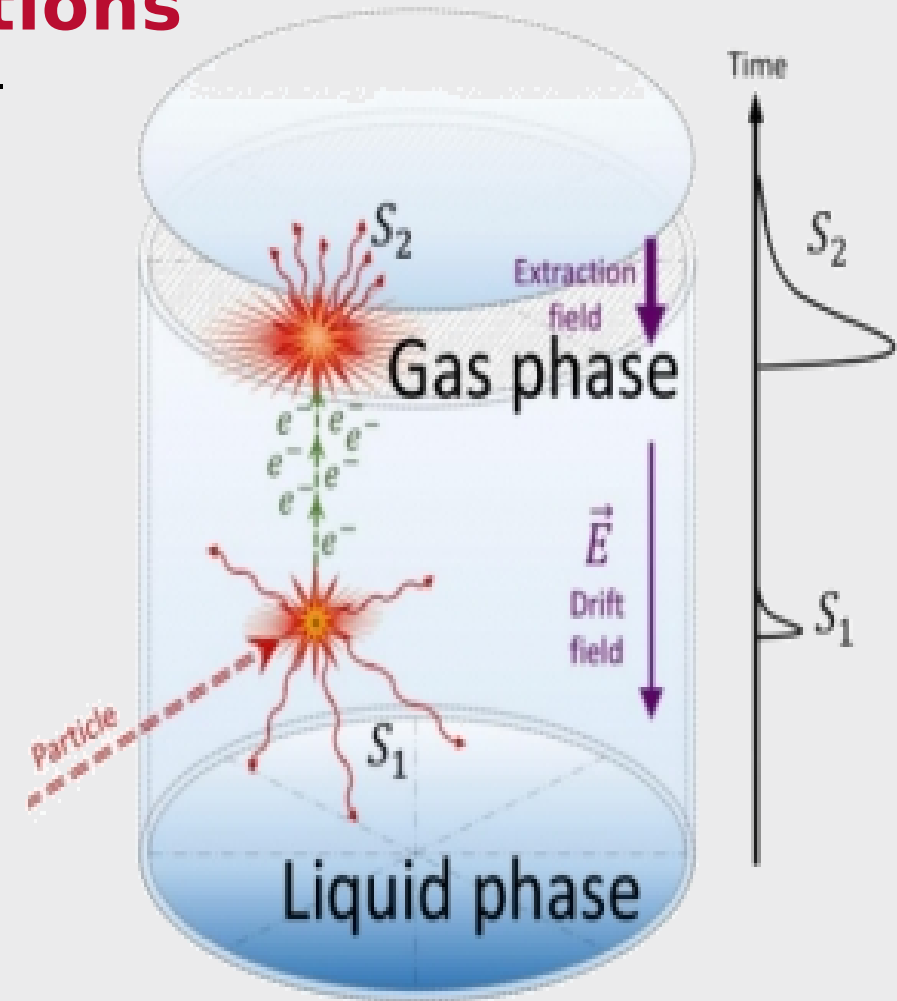
Fluorescence	Scintillation	
1,1,4,4-tetraphenyl-1,3-butadiene ( <b>TPB</b> ) <small>J. M. Corning, et al., JINST 15 (3) C03046.</small>	zinc tungstate ( <b>ZnWO<sub>4</sub></b> ) <small>P. C. F. Di Stefano et al. NIM A.700 40</small>	 <p>5mm</p> <p>32mm</p> <p>24mm</p>
poly (methyl methacrylate) ( <b>PMMA or Acrylic</b> ) <small>E. Ellingwood et al. NIM A. 1039 167119</small>	bismuth germanate ( <b>B<sub>4</sub>G<sub>3</sub>O<sub>12</sub></b> ) <small>M-A Verdier et al. Phys Rev. B. 84 214306</small>	
<b>Pyrene-doped polystyrene</b> <small>H. Benmansour et, al. JINST 6, P12029</small>	pure cesium iodide ( <b>CsI</b> ) <small>Michael Clark et al. NIM A. 901 6</small>	
poly(ethylenedioxythiophene) polystyrene sulfonate ( <b>Clevios</b> )	Calcium tungstate ( <b>CaWO<sub>4</sub></b> ) <small>Moritz Von Sivers, et al. JAP, 118 164505</small>	

TPB sample attached to cryostat cold finger illuminated by soft UV light.

**Clevios** is an optically transparent, conductive polymer. This material can be coated to substrates to create a **thin conductive surface**. Applications in photovoltaic cells, electroluminescent lamps, and **transparent electrodes**.

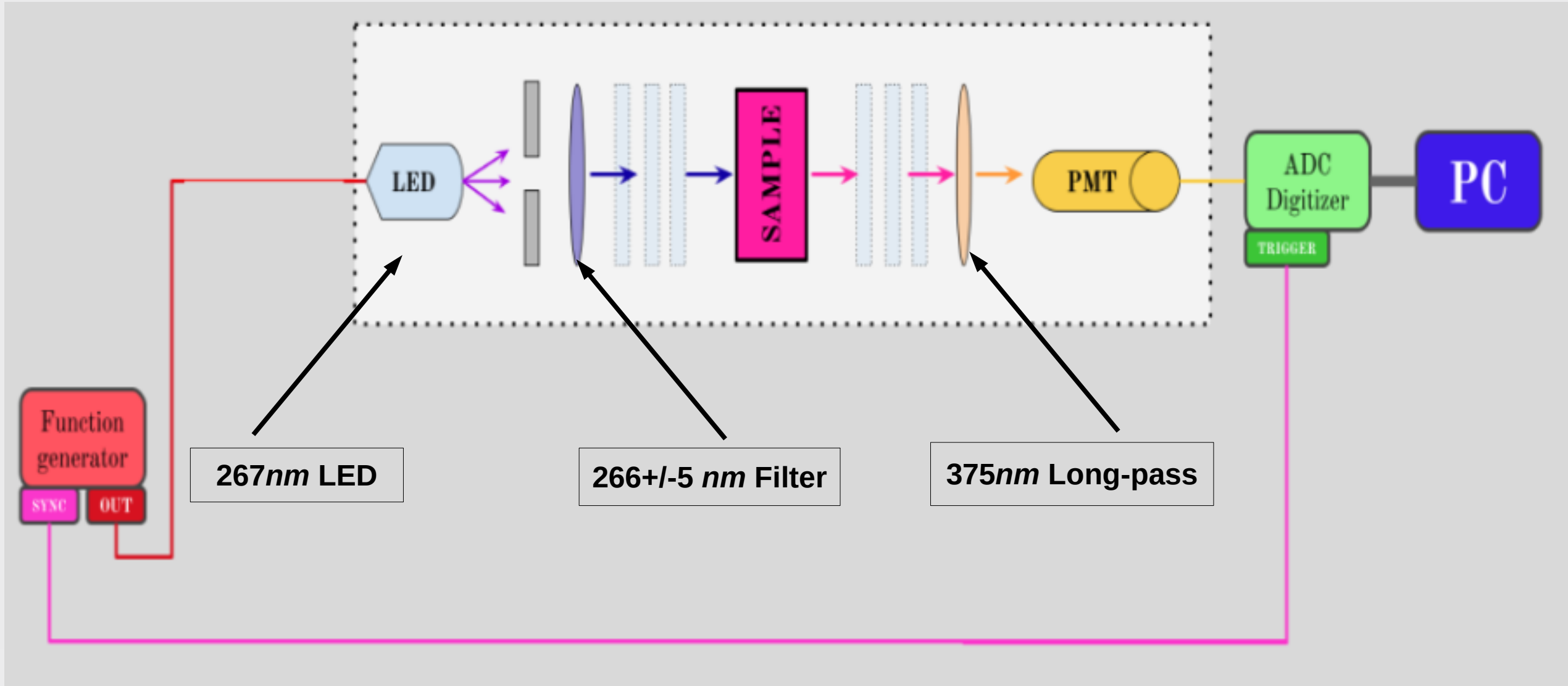
## Experimental Motivations

- Rare event searches, such as DEAP-3600 and DarkSide-20k, make use of 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) to shift the **scintillation light** from cryogenic liquids from ultraviolet to visible light.
- Detector materials, such as acrylic, can introduce a UV-stimulated fluorescent background.
- Literature<sup>1</sup> suggests that **Clevios**, a conductive material which will be used to generate the electric field for the DarkSide-20k TPC, may also exhibit UV-stimulated fluorescence.
- It is necessary to understand the photoluminescent properties of these materials and how they **change with temperature**.



DarkSide-20k TPC schematic

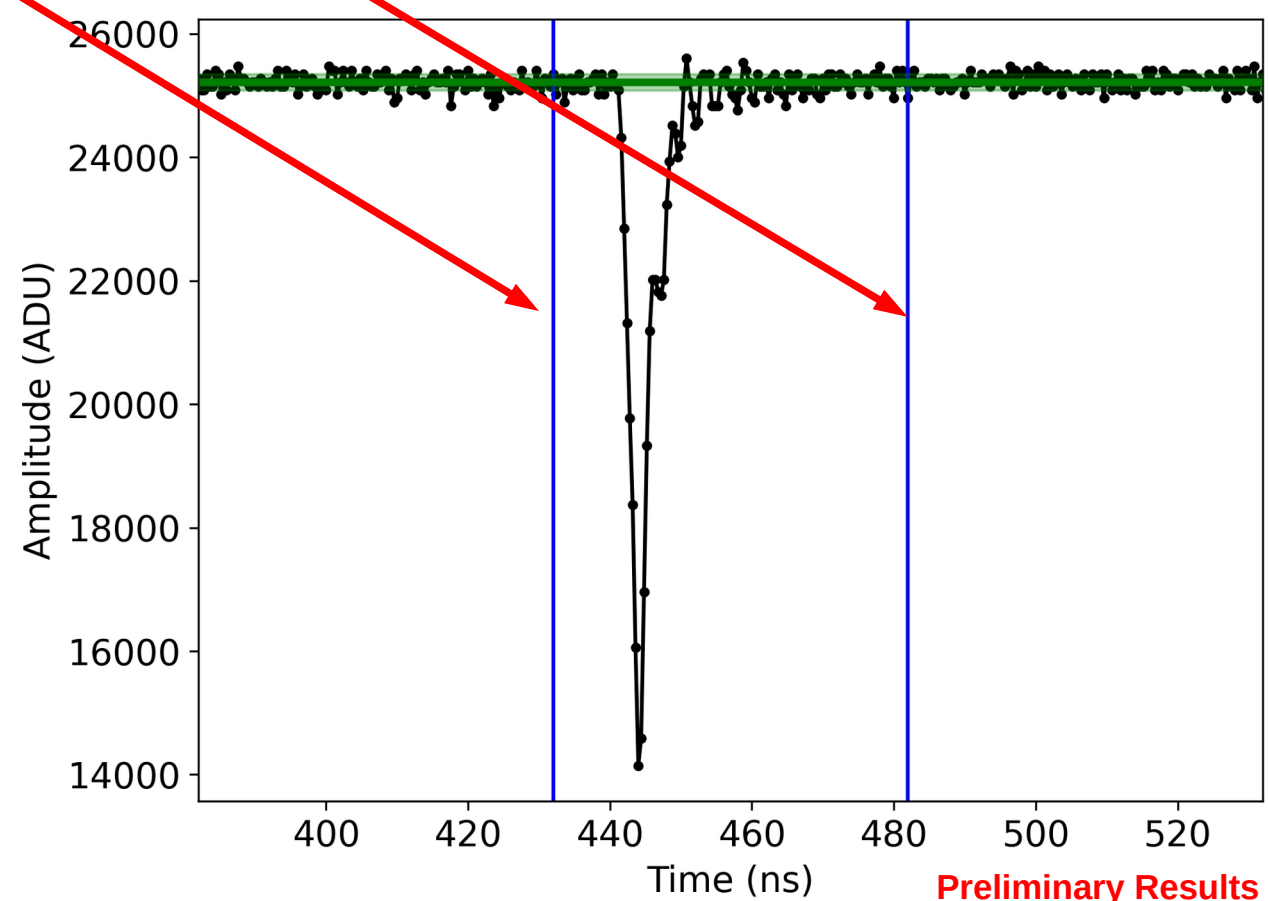
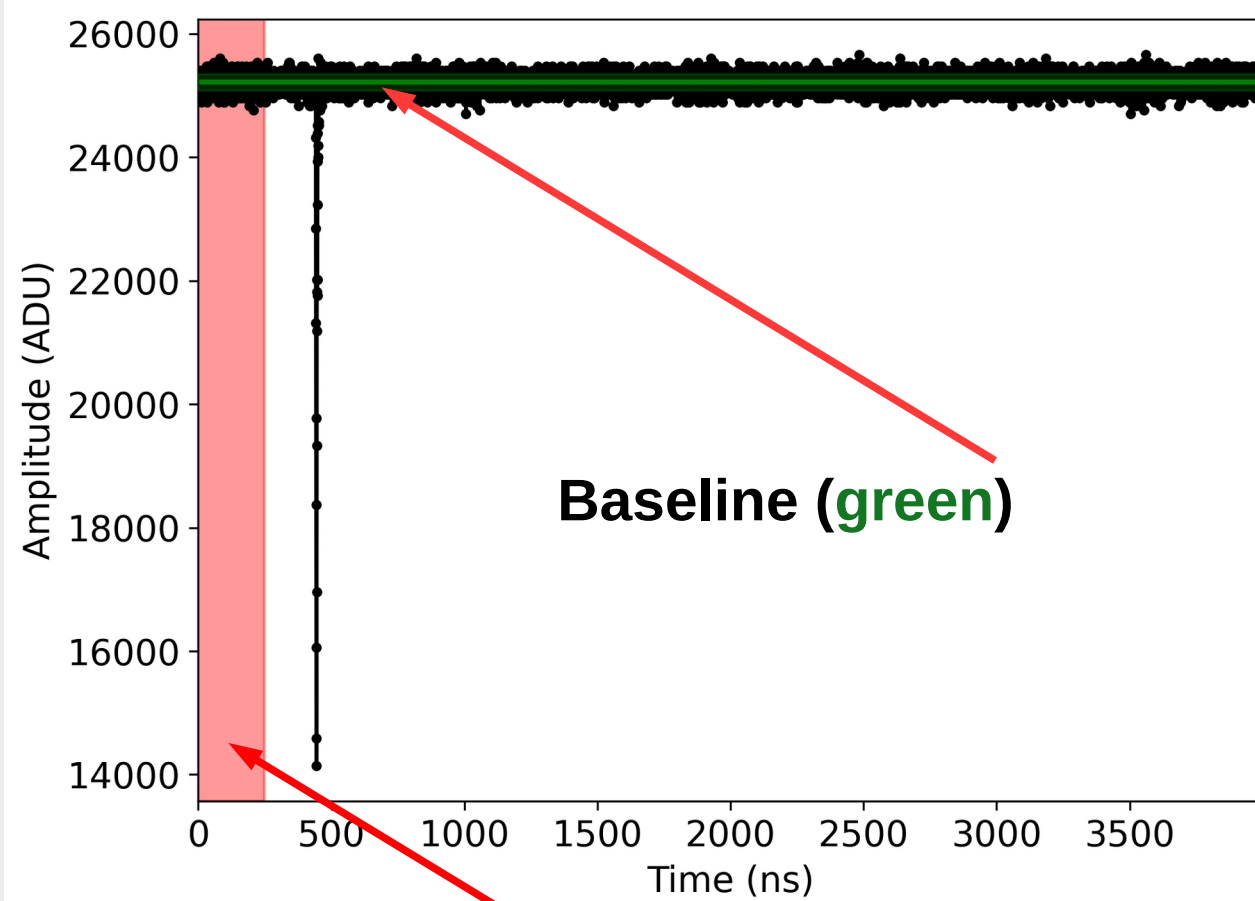
# 5 Experimental Schematic



**\*Note:** In **spectral analysis**, the PMT is replaced with the spectrometer and the LED is run in continuous mode.

# 6 Typical Pulse Registered by PMT (Single Electron)

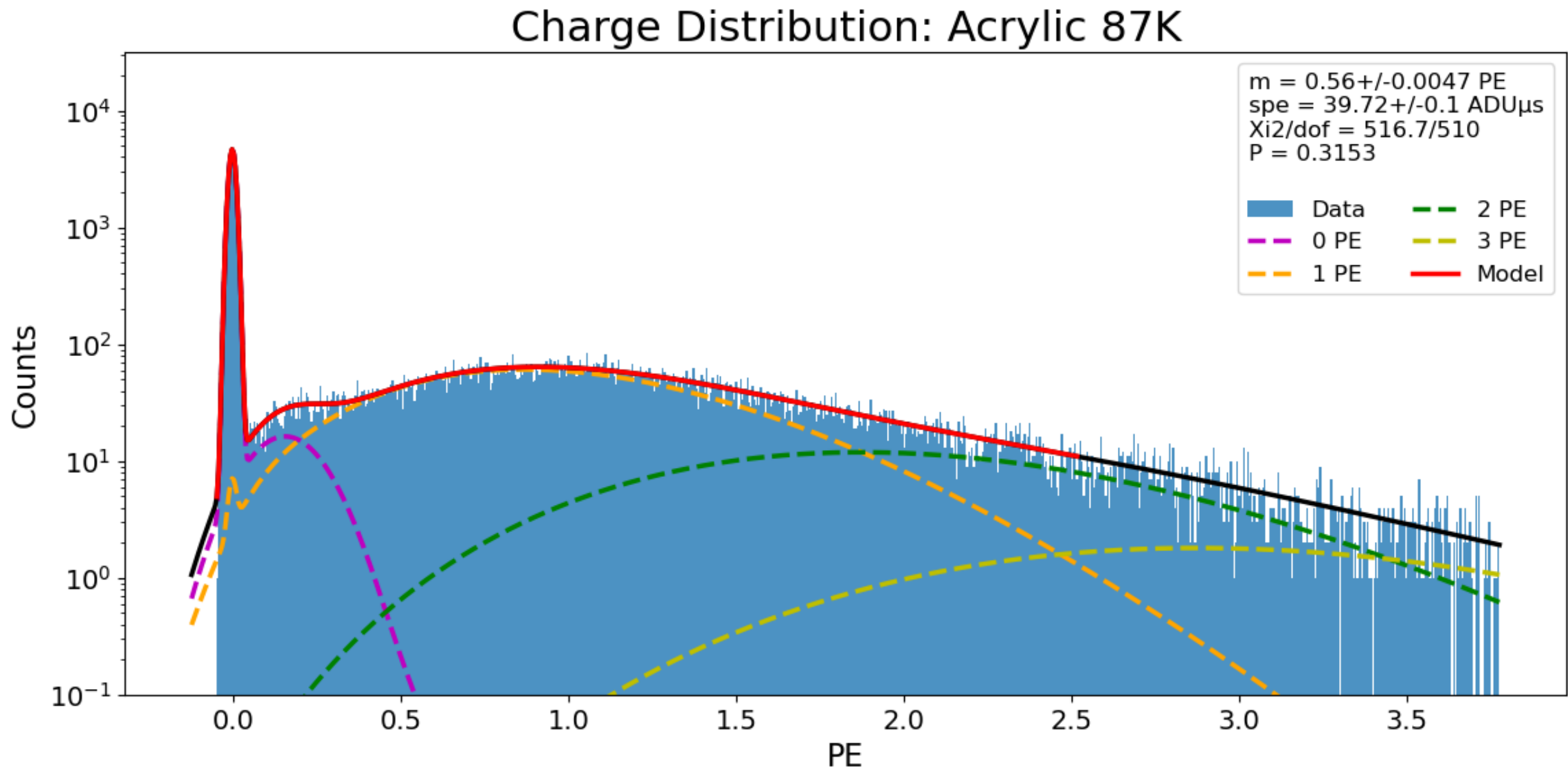
Integration Region (50ns)



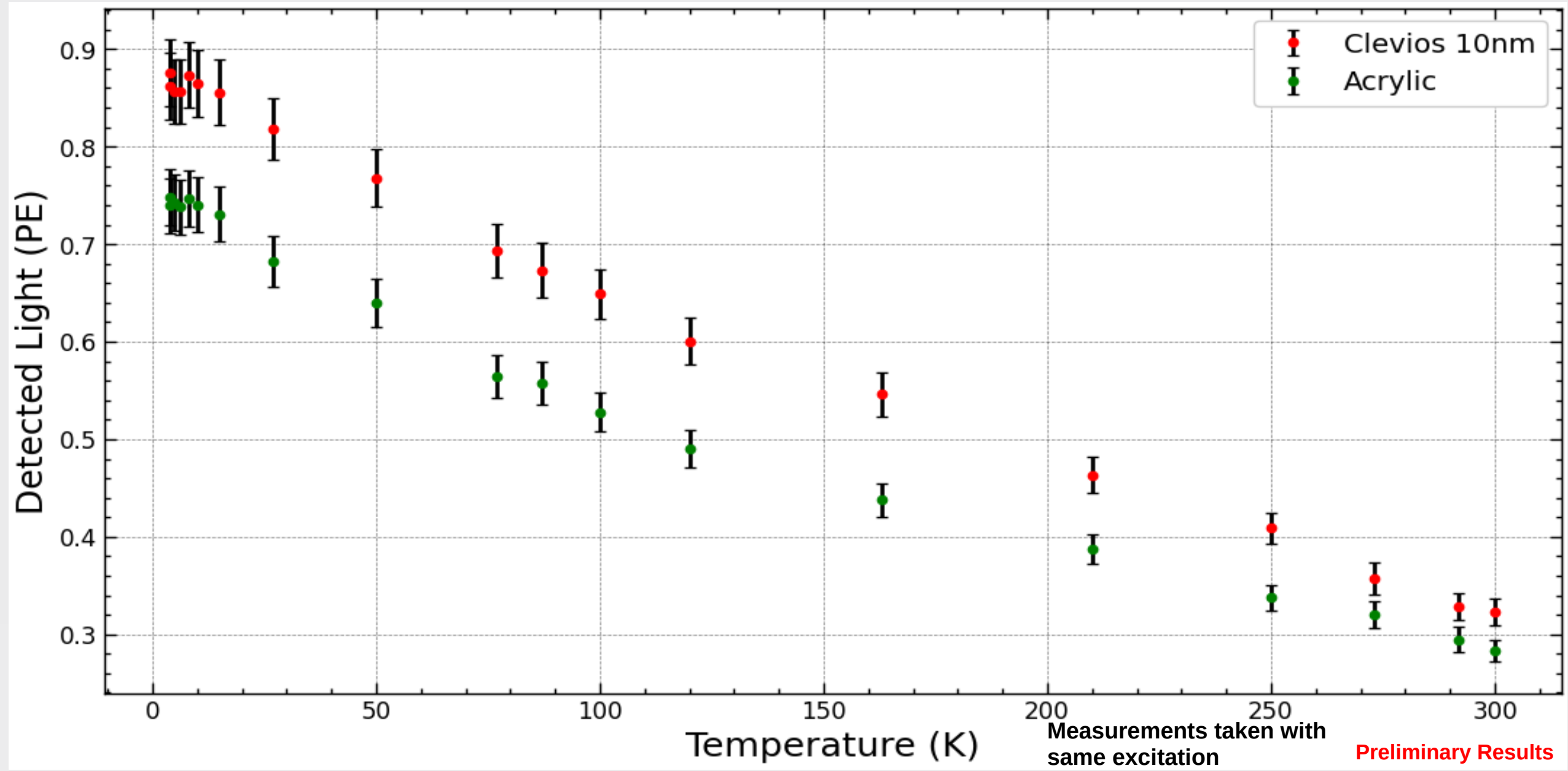
Pretrigger region

Preliminary Results

# Single Photoelectron Distribution: Blank Acrylic Substrate



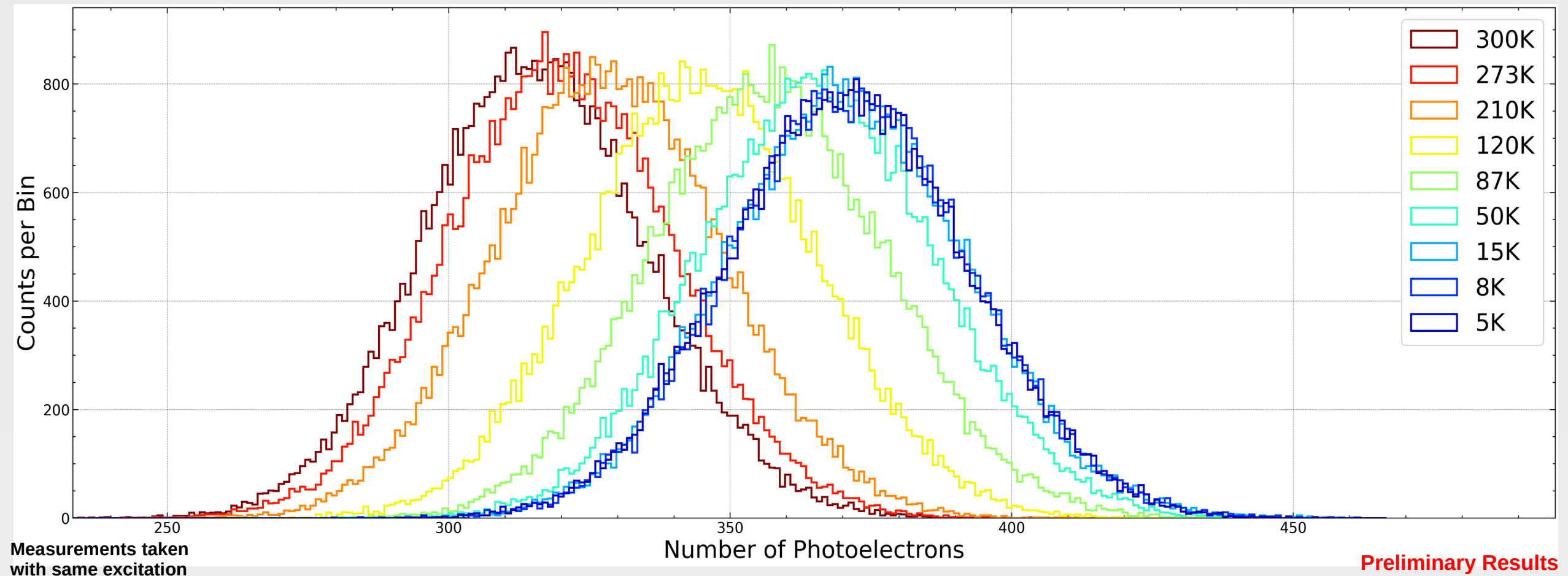
# Detected light vs Temperature: Clevios & Acrylic





## 9 Highly Fluorescent Samples: TPB

- Recall that the motivation of these measurements is to understand optical processes taking place in a rare event detector, such as DEAP-3600 and Darkside-20K.
- One material of interest is the **wavelength shifter** TPB, which transforms the **128nm** liquid argon scintillation light into visible light with peak emission of **~420nm**.



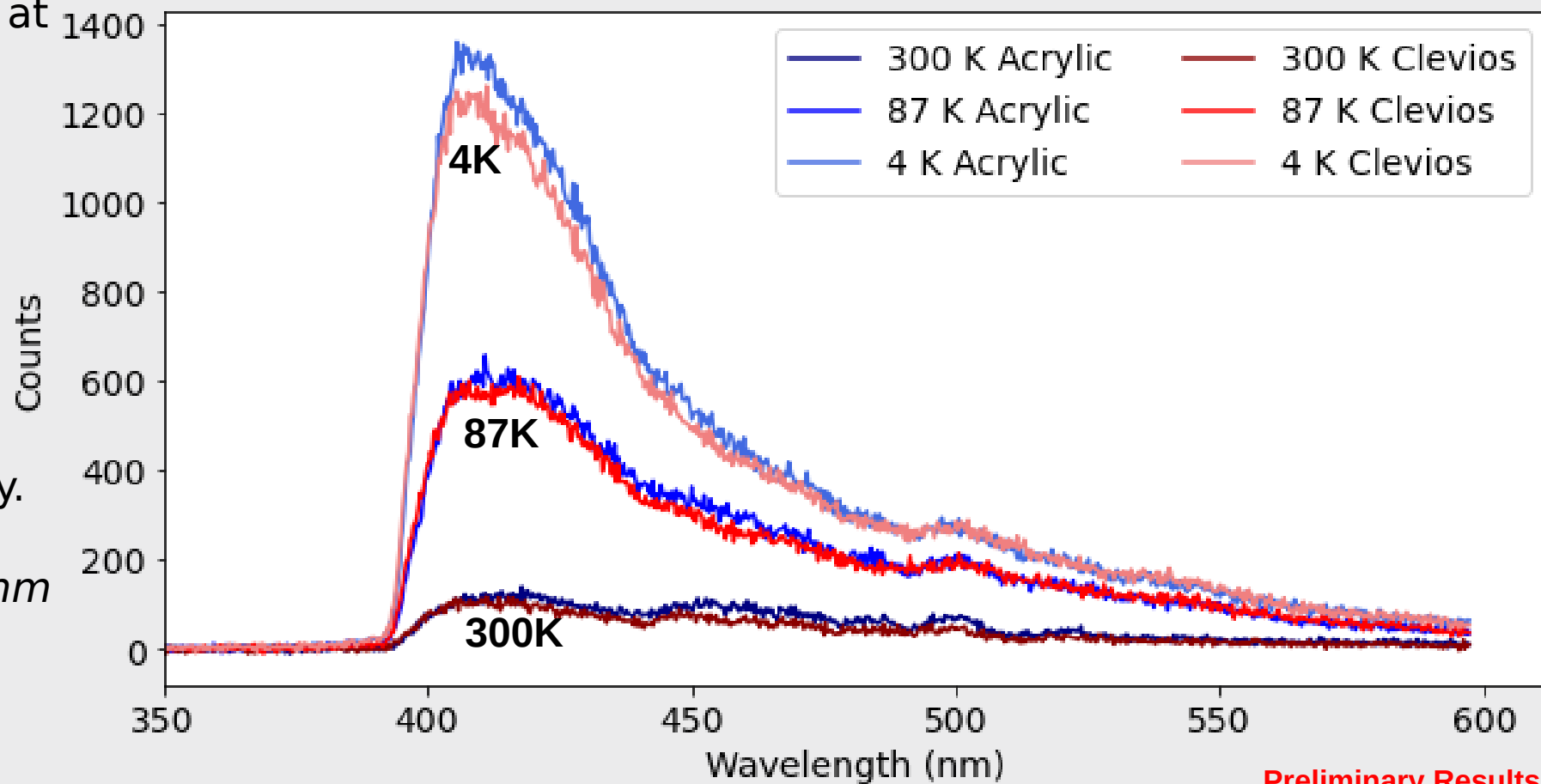
# Cryostat: Spectral Measurements

Spectral features, obscured at room temperature, reveal themselves at cryogenic temperatures.

**Blue** and **red** curves show the acrylic and Clevios spectral results, respectively.

Spectra are taken with 260nm LED in continuous mode.

Note: minor intensity differences in spectra should not be considered significant.



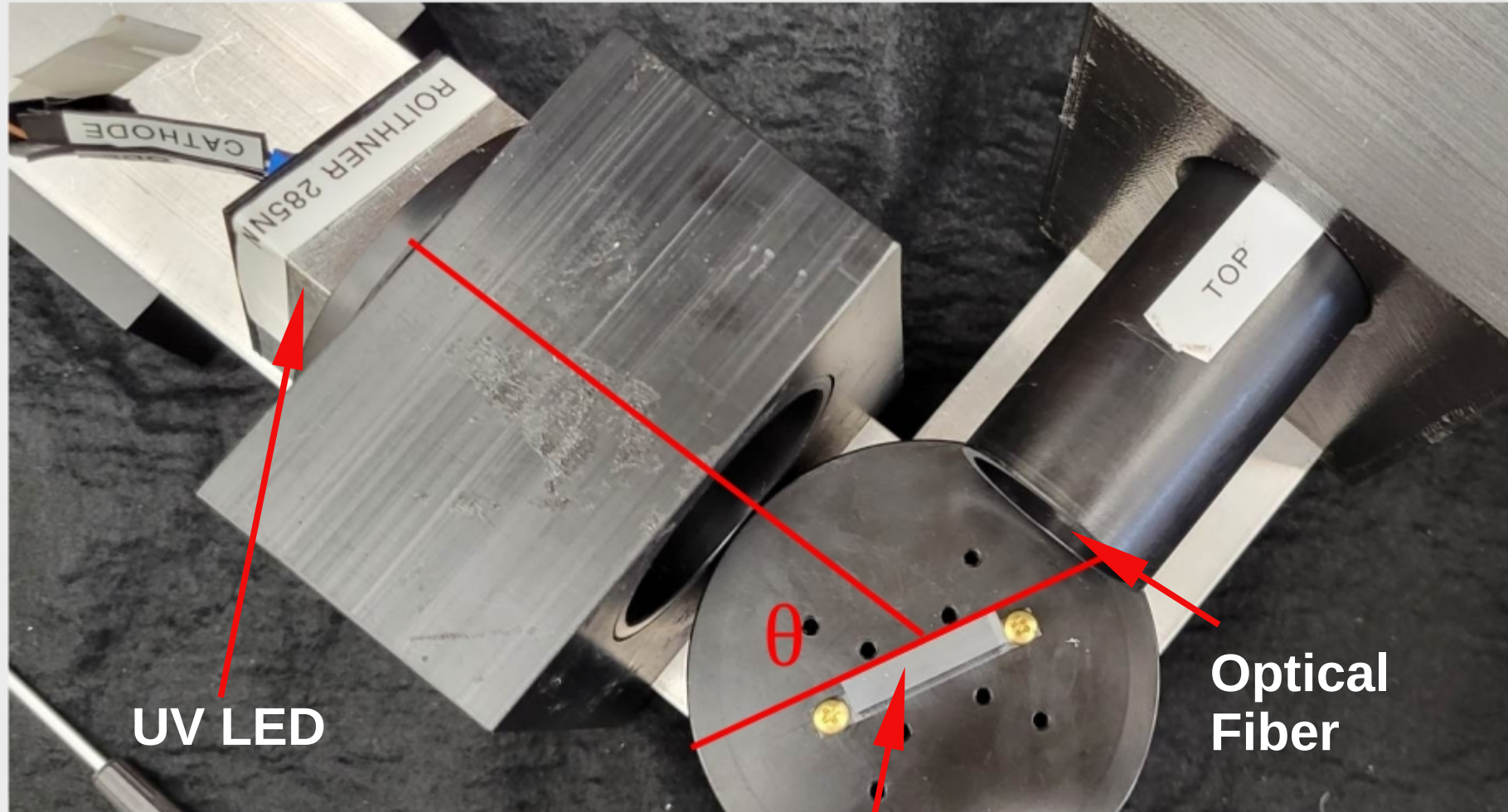
Preliminary Results

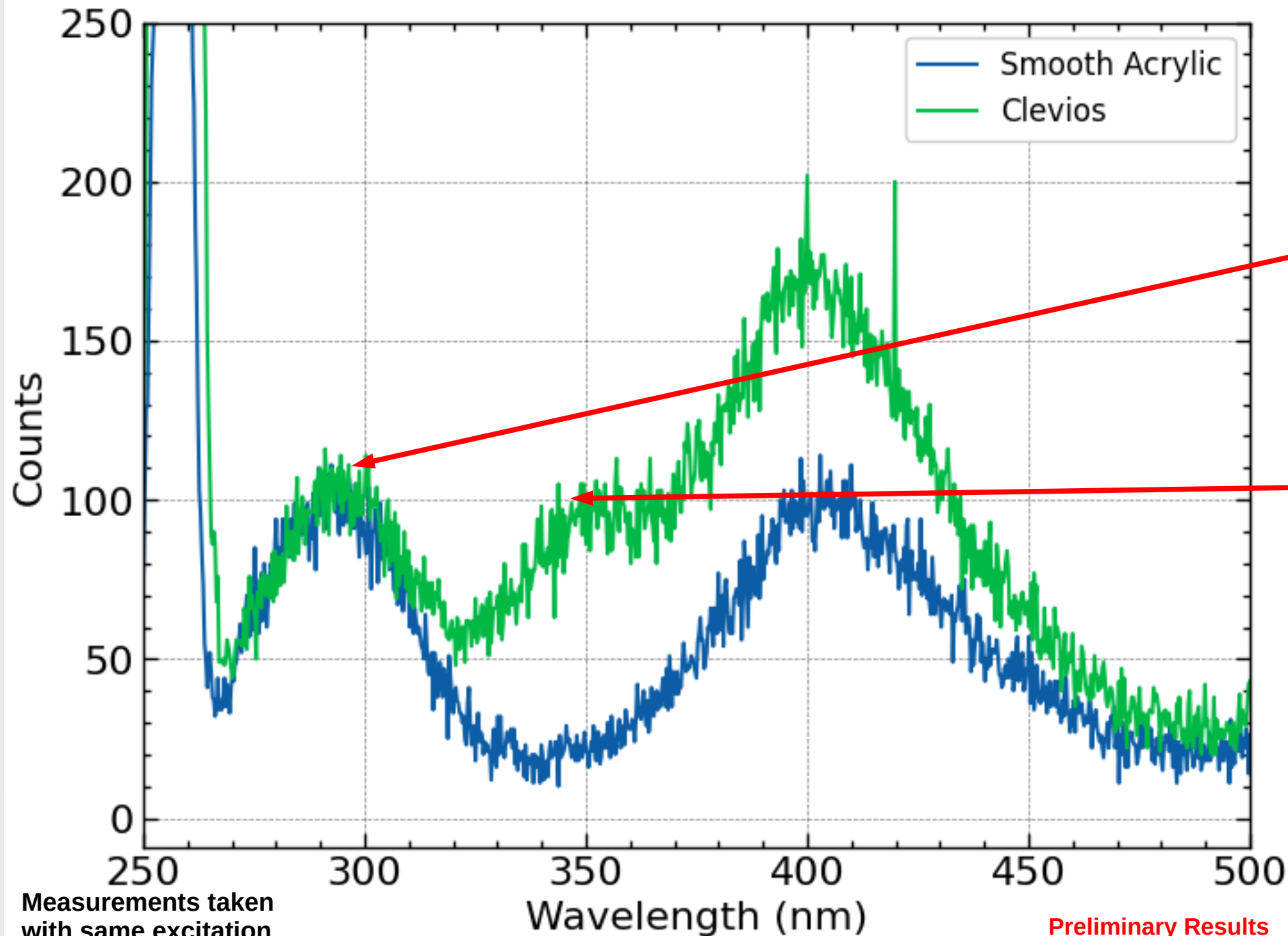
# 11 Same Side Spectral Measurements

Literature suggests that Clevios may **fluoresce** at **ultra-violet** wavelengths.

Substrate would absorb light at these wavelengths, hence a new configuration is required to measure fluorescence from the surface of the sample.

The dual arm set-up allows for this measurement at room temperatures





Unexpected acrylic feature (possible **crosslink** feature? Reference [here](#))

Broad UV feature of **Clevios** (likely polystyrene sulfonate, source [here](#) and [here](#))

Measurements taken with same excitation

Preliminary Results



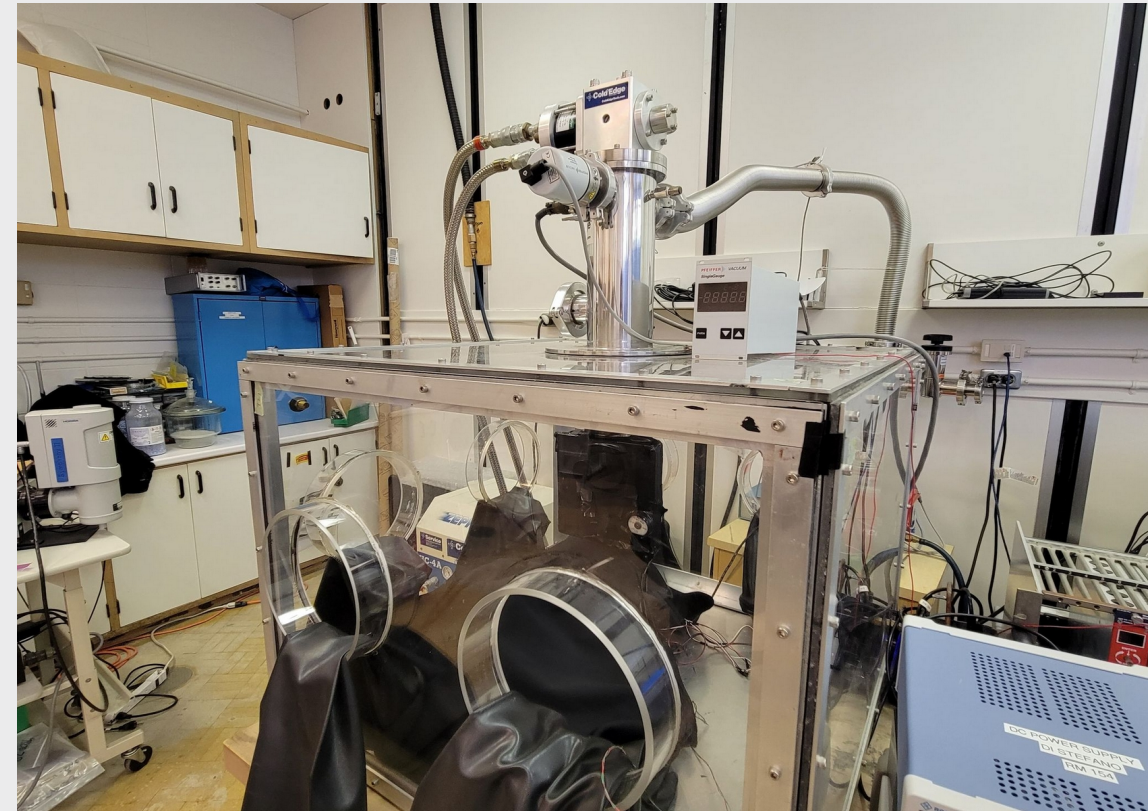
## Conclusion

The optical cryostat experiment at Queen's University has demonstrated its abilities to test optical behavior of samples at cryogenic temperatures under vacuum.

Time-resolved measurements of acrylic and Clevios reveal that Clevios of thicknesses on the order of  $\sim 10\text{nm}$  does not exhibit substantial fluorescence.

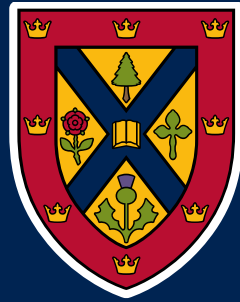
Similar measurements were performed on samples of thickness on the order of  $\sim 100\text{nm}$  and yields similar results.

Experiments, including DarkSide-20k can safely implement this new material without fear of introducing a significant amount of background light.



Top: Cryostat  
Left: Delta Diode  
267

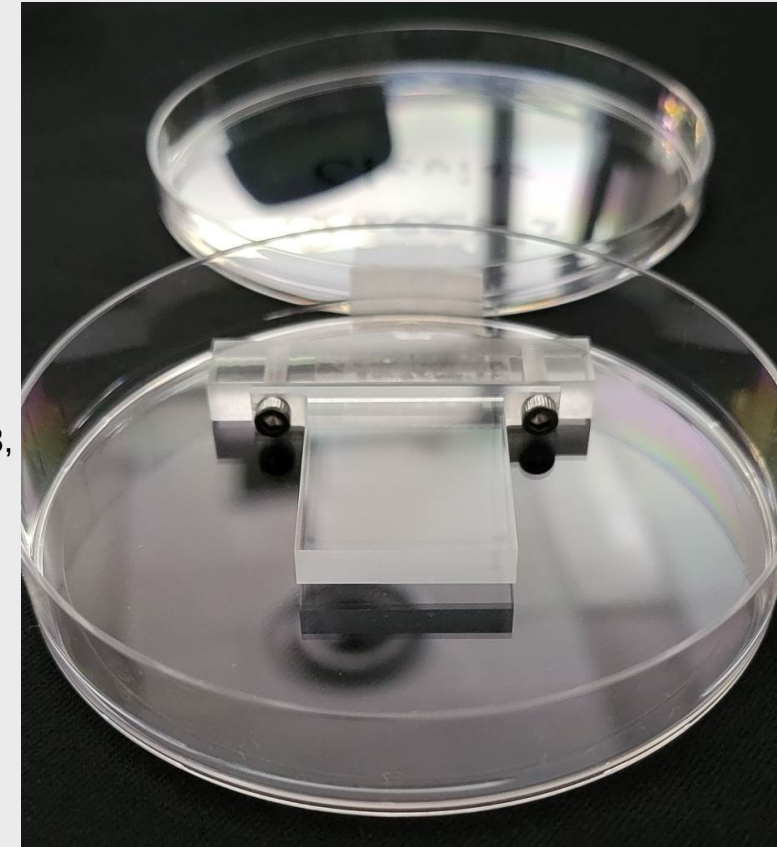




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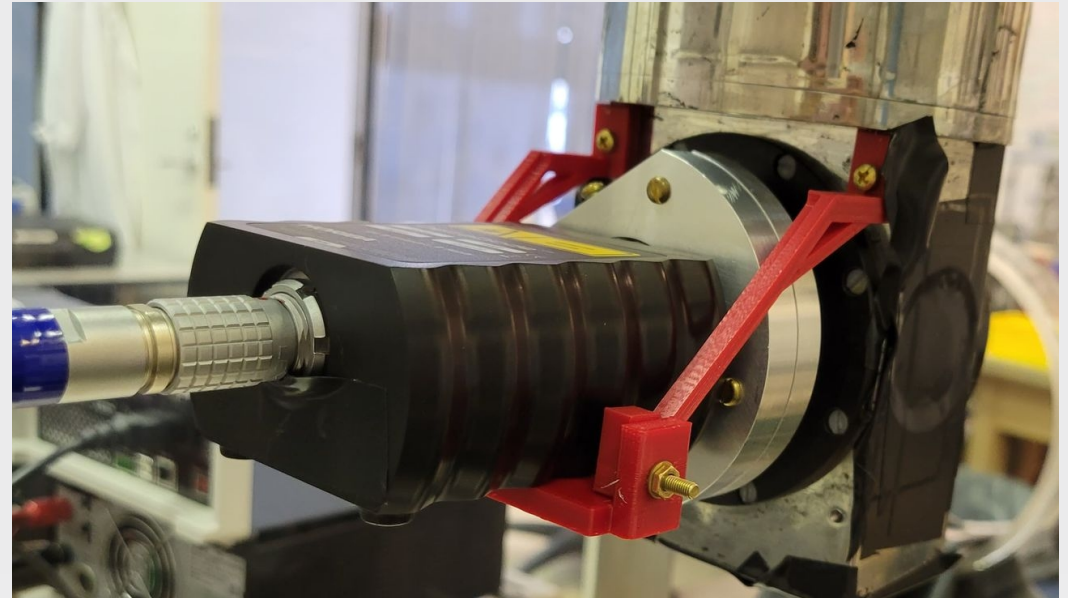
# References

- C. Lally et al. UV quantum efficiencies of organic fluors. Nucl. Instr. Meth.197 B, 117(4):421–427, Oct. 1996.
- E. Ellingwood et al. Ultraviolet-induced fluorescence of poly(methyl methacrylate) compared to 1,1,4,4-tetraphenyl-1,3-butadiene down to 4 k. Nucl. Instrum. Methods Phys. Res. A, 1039:167119, sep 2022
- H. Benmansour, et al., Fluorescence of pyrene-doped polystyrene films from room temperature down to 4 K for wavelength-shifting applications, J. Instrum. (Oct. 2021).
- J. M. Corning, et al., Temperature-dependent fluorescence emission spectra of acrylic (PMMA) and tetraphenyl butadiene (TPB) excited with UV light, J. Instrum. 15 (3) (2020) C03046. arXiv:1912.02073, doi:10.1088/1748-0221/15/03/C03046.
- P.-A. Amaudruz et al. Design and construction of the DEAP-3600 dark matter detector. Astropart. Phys, 108:1–23, mar 2019.
- R. Francini, VUV-Vis optical characterization of Tetraphenyl-butadiene films on glass and specular reflector substrates from room to liquid Argon temperature, J. Instrum 8 (2013) 09006. doi:https://doi.org/10.1088/1748-0221/8/09/P09006.
- S. Beavan, P. Hackett, D. Phillips, Phosphorescence of carbonyl compounds produced by thermal and photo-oxidation of polybutadiene, European Polymer Journal 10 (10) (1974) 925–932. doi:https://doi.org/10.1016/0014-3057(74)90030-5.
- S. Tokar, I. E. Chirikov-Zorin, I. Sykora, and M. Pikna. Single Photoelectron Spectra Analysis for the Metal Dynode Photomultiplier, January 1999
- T. Koyama et al. Photoluminescence of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in the visible region. J. Mater. Chem. C, 3(32):8307–8310, 2015



# References cont.

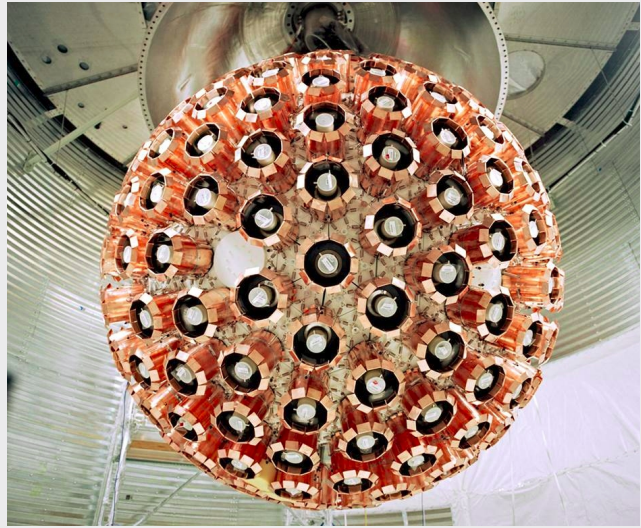
- M. Simoncic, J. Hritz, and M. Luksic. Biomolecular Complexation on the “Wrong Side”: A Case Study of the Influence of Salts and Sugars on the Interactions between Bovine Serum Albumin and Sodium Polystyrene Sulfonate. *Biomacromolecules*, 23(10):4412–4426, October 2022. Publisher: American Chemical Society.
- Y. W. Park et al. Electrical conductivity of highly-oriented-polyacetylene. *Solid State Commun.*, 65(2):147–150, January 1988
- A. P. Dorado and Inés F. Piérola. Mobility of knots in polyethylacrylate networks. *Polym. Bull.*, 34(5):605–613, September 1995
- M-A Verdier et al. Scintillation properties of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> down to 3 K under  $\gamma$  rays. *Nucl. Instrum. Methods Phys. Res. B*, 84, December 2011.
- M. Von Sivers, , et al. Low-Temperature Scintillation Properties of CaWO<sub>4</sub> Crystals for Rare-Event Searches. *J. Appl. Phys.*, 118, October 2015.
- P. C. F. Di Stefano et al. Counting photons at low temperature with a streaming time-to-digital converter. *Nucl. Instrum. Methods Phys. Res. A*, 700:40–52, February 2013. arXiv:1207.2448 [physics].
- M. Clark et al. Particle detection at cryogenic temperatures with undoped CsI. *Nucl. Instrum. Methods Phys. Res. A*, 901:6–13, September 2018. arXiv:1709.04020 [physics].



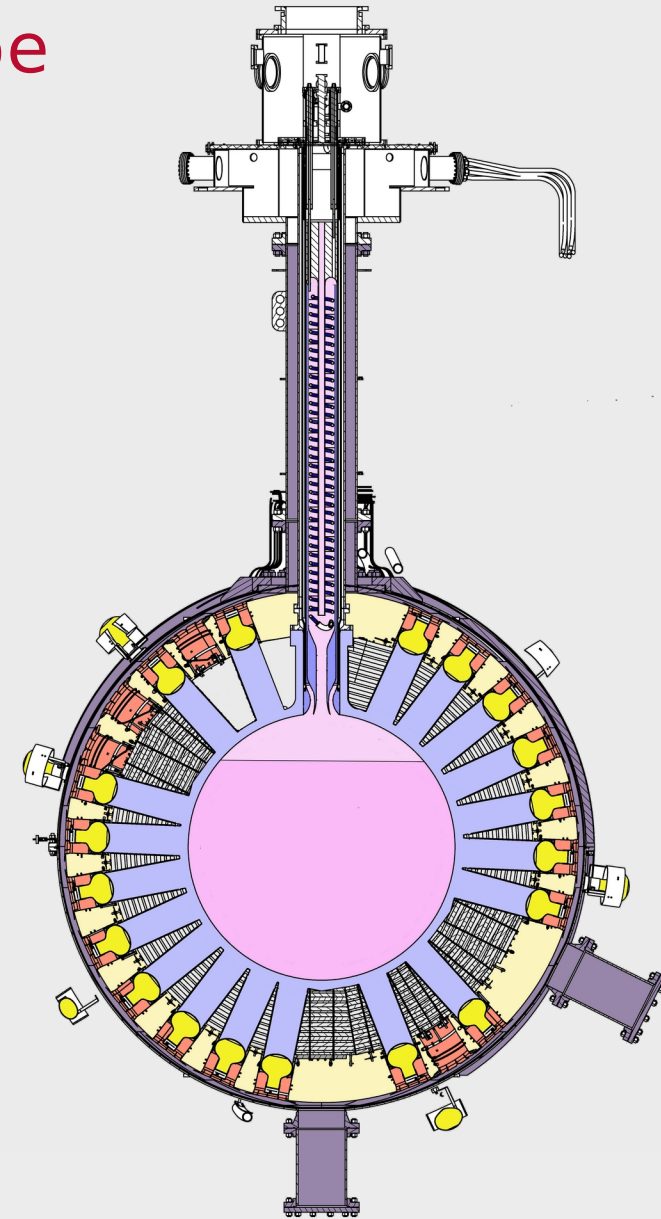


# Backup Slides

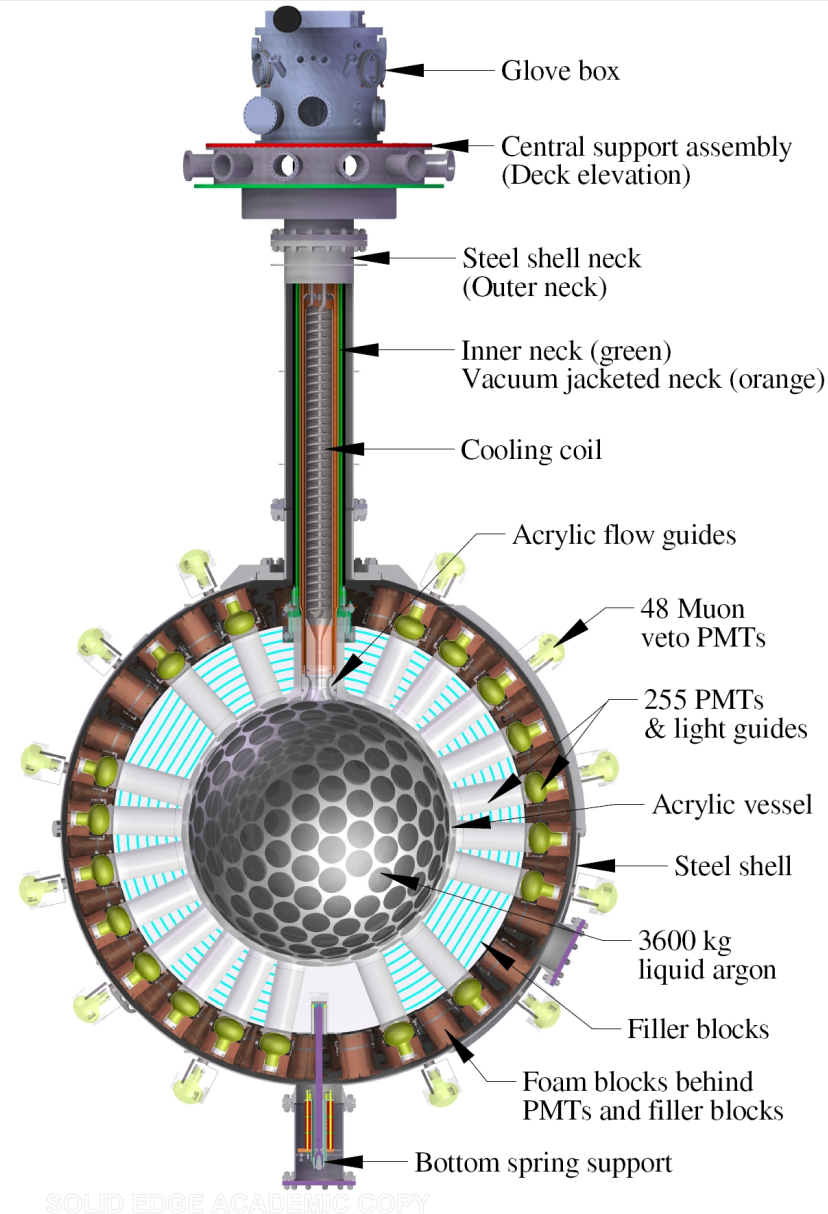
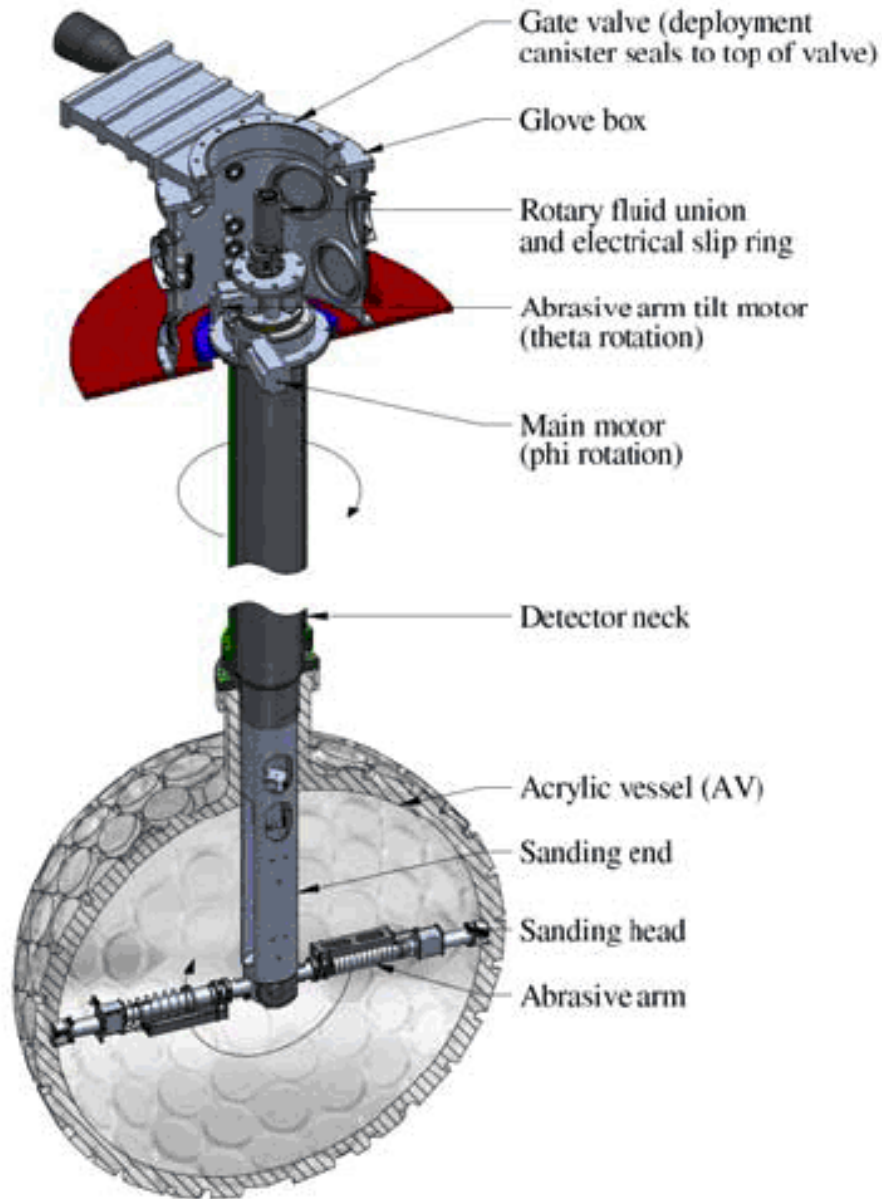
# Dark Matter Experiment with Argon Pulse shape discrimination (**DEAP-3600**)



- Single phase liquid argon (LAr) detector optimized to detect **128nm LAr scintillation light** produced during nuclear/electron recoil (NR/ER) events.
- LAr is preferred due to substantial particle identification capabilities. ER events preferentially excite the argon to the triplet state (lifetime of  $\sim 1500\text{ns}$ ) where NR events excite the argon to the singlet state (lifetime of  $\sim 6\text{ns}$ ).
- The **wavelength is shifted from 128nm to 420nm** light thanks to **TPB**. Important for PMTs to capture this light.



# Detailed Diagram of DEAP3600



Images take from the DEAP3600 website:  
<http://deap3600.ca/deap-3600-detector/>

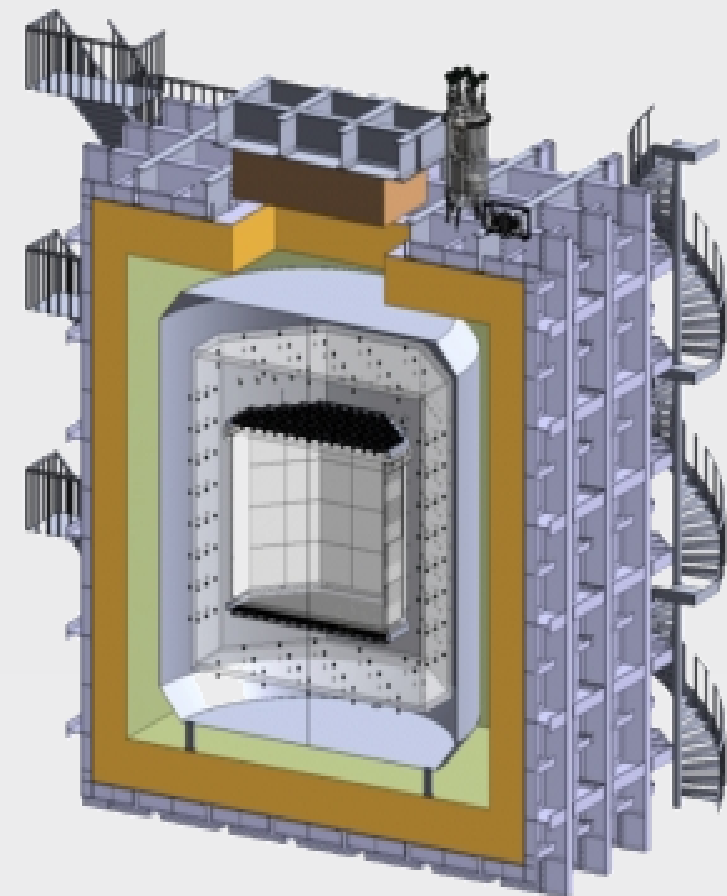
Left: schematic of resurfacer to sand the inner detector

Right: full overview of detector

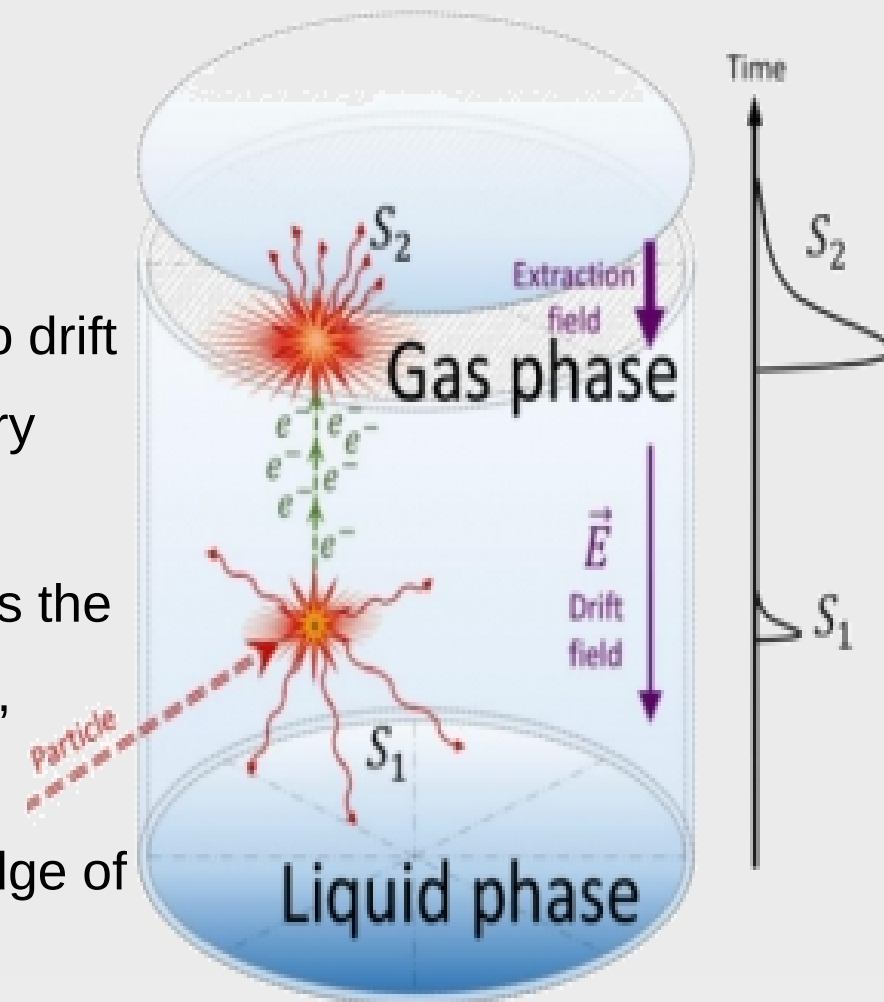


## Darkside-20K

- 20 tonne dual phase liquid argon (LAr) detector.
- Currently in development stage, will be located at Gran Sasso
- **Initial interaction** between a particle and the detector produce **scintillation light** and **ionization electrons**.



- An electric field allows the electrons to drift upwards towards a liquid/gas boundary region.
- **Electro-luminescence** is produced as the electron travels in the gaseous region, producing a second signal .
- Detection of both signals and knowledge of the electron drift time, allows for **reconstruction the position** of the initial event.



## 21 The Data Acquisition

Fluorescent light from the sample travels through the bandpass filter and reaches a photomultiplier tube (PMT) (Hamamatsu R6095-100). This PMT is primarily sensitive to visible light. We have an additional, UV sensitive PMT, sensitive down to  $200\text{nm}$  (Hamamatsu R7449).

Photons may either capture on the photocathode via the photoelectric effect or may travel straight through the PMT.

The photoelectrons (PEs) generated on the photocathode create a measurable signal at the anode of the PMT governed by the gain of the PMT.

This signal is fed into a digitizer (PXIE 5162) where the signal is converted to a binary file.

The binary file is then processed offline to determine necessary values for data analysis, such as the baseline, integral, saturation limit, etc...

Alternatively, an optical fiber connected to a spectrometer can replace the PMT to make wavelength spectral measurements of a sample. This data is stored in a text file.



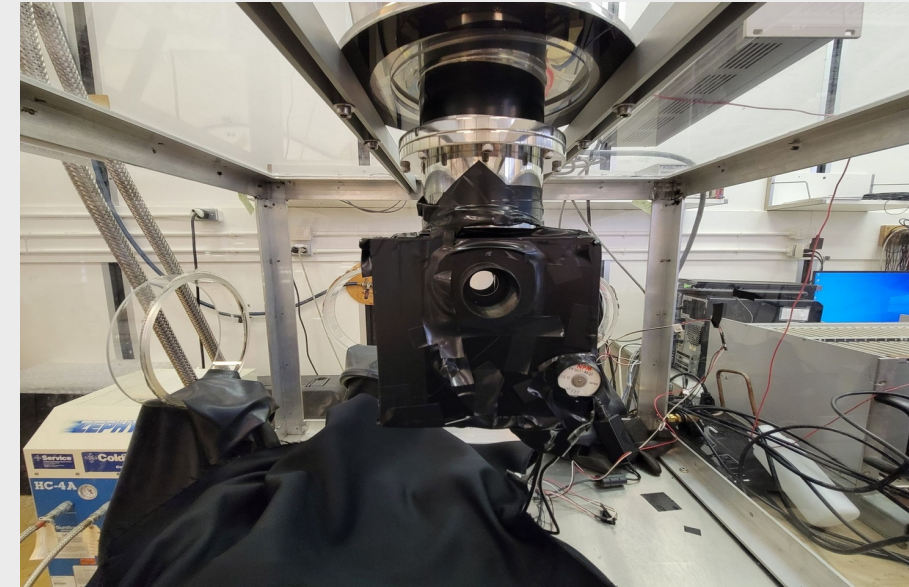
## The Optics

Previous studies have been carried out with a UV LED with wavelength of  $285nm$ , pulsed for  $\sim 10ns$  at a frequency of  $50Hz$ .

Current developments and upgrades are ongoing with the optics system. Shorter wavelength LEDs with stable output intensity and pulse width, are being installed, calibrated, and tested.

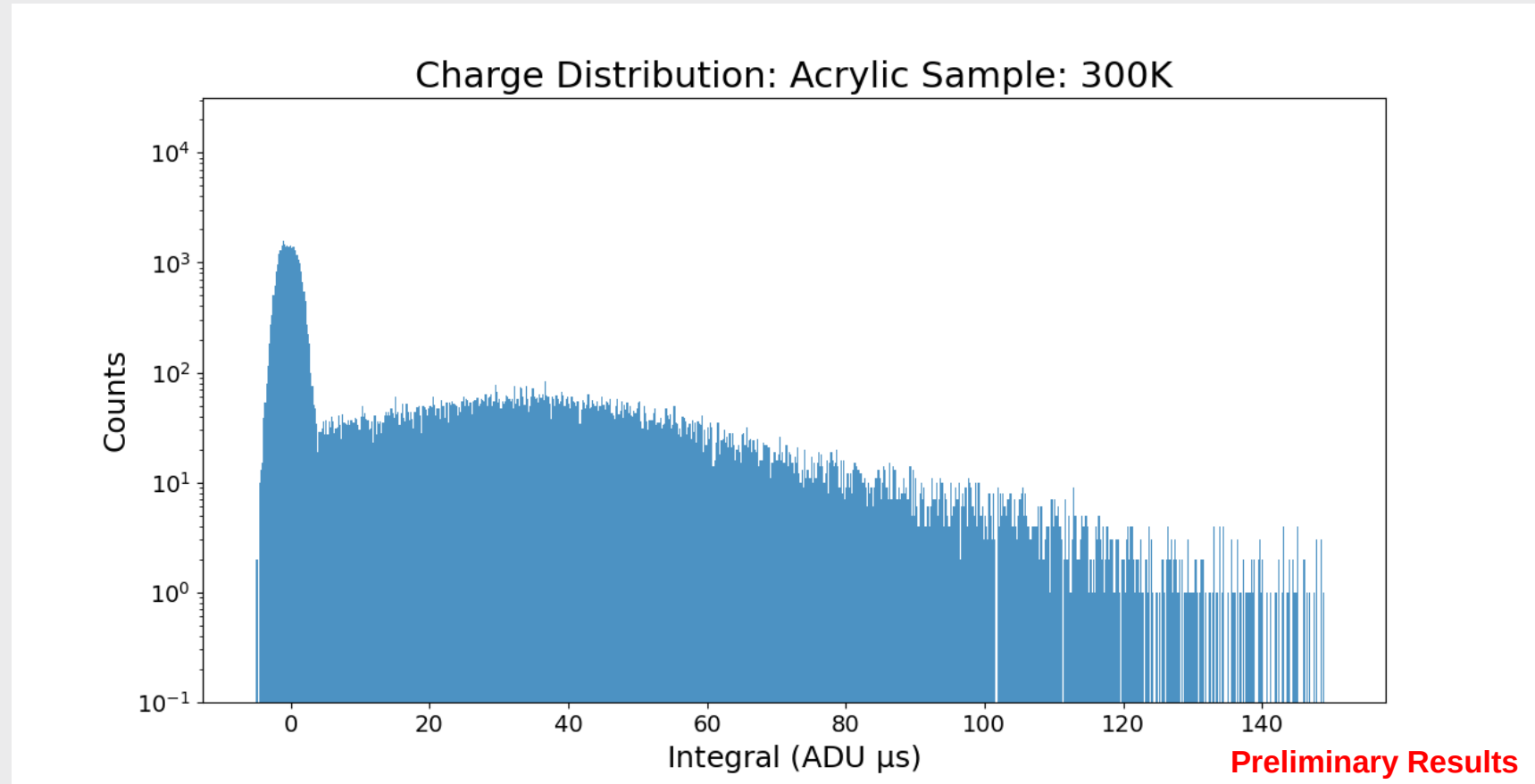
Filters are implemented before the light reaches the sample to ensure that the excitation light contains only the correct wavelength of light (no stray light/broad emission features).

Filters are also implemented after the sample to remove reflected light from the LED and allows light between  $360$  and  $660nm$  to pass.



# Individual SPE Data Set: Building the Model

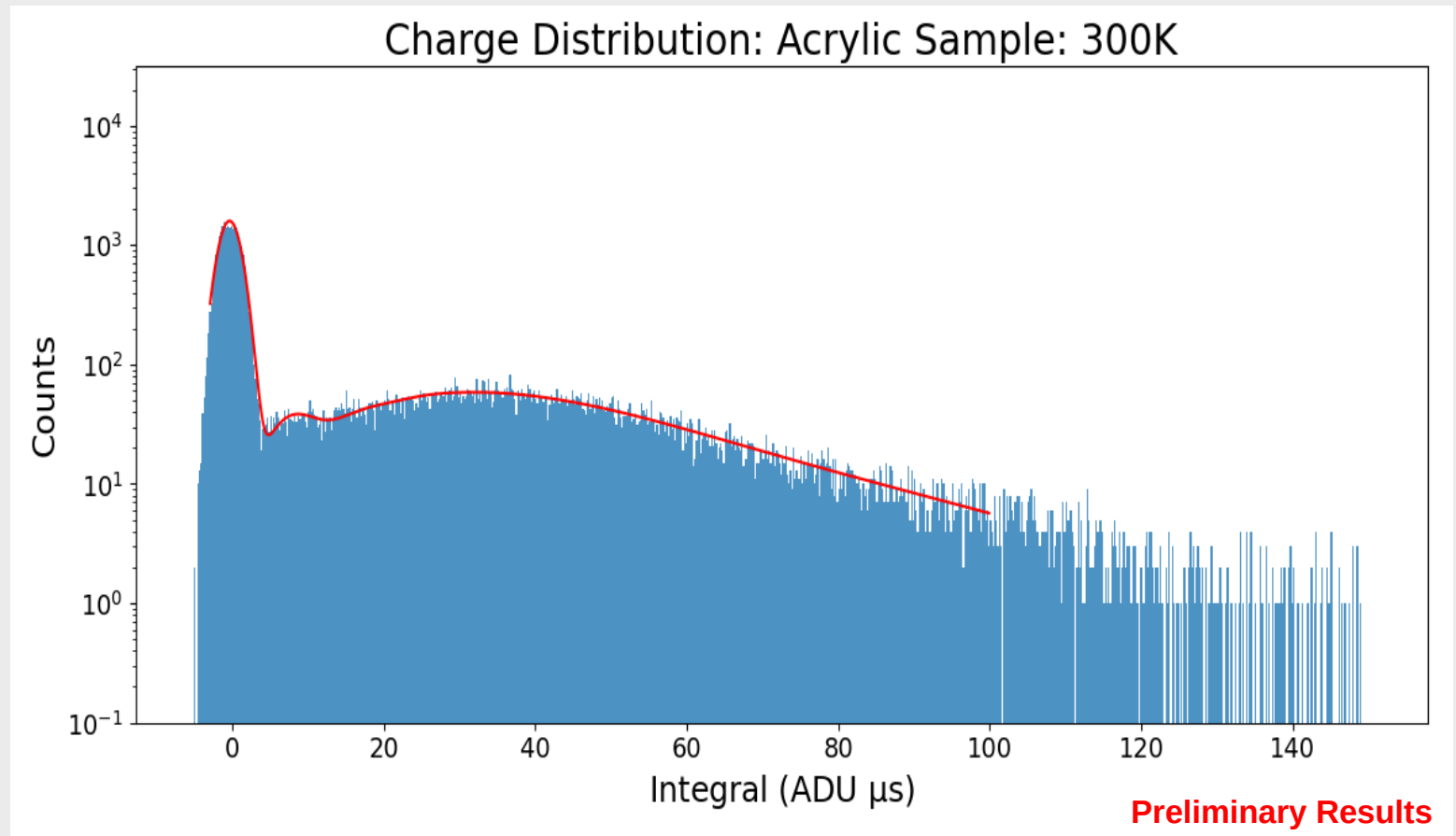
- **Step One: plot the data**



## 24 Individual SPE Data Set: Building the Model

- **Step One: plot the data**
- **Step Two: Determine model parameters by minimization chi2 method and plot the resulting modeled charge distribution.**

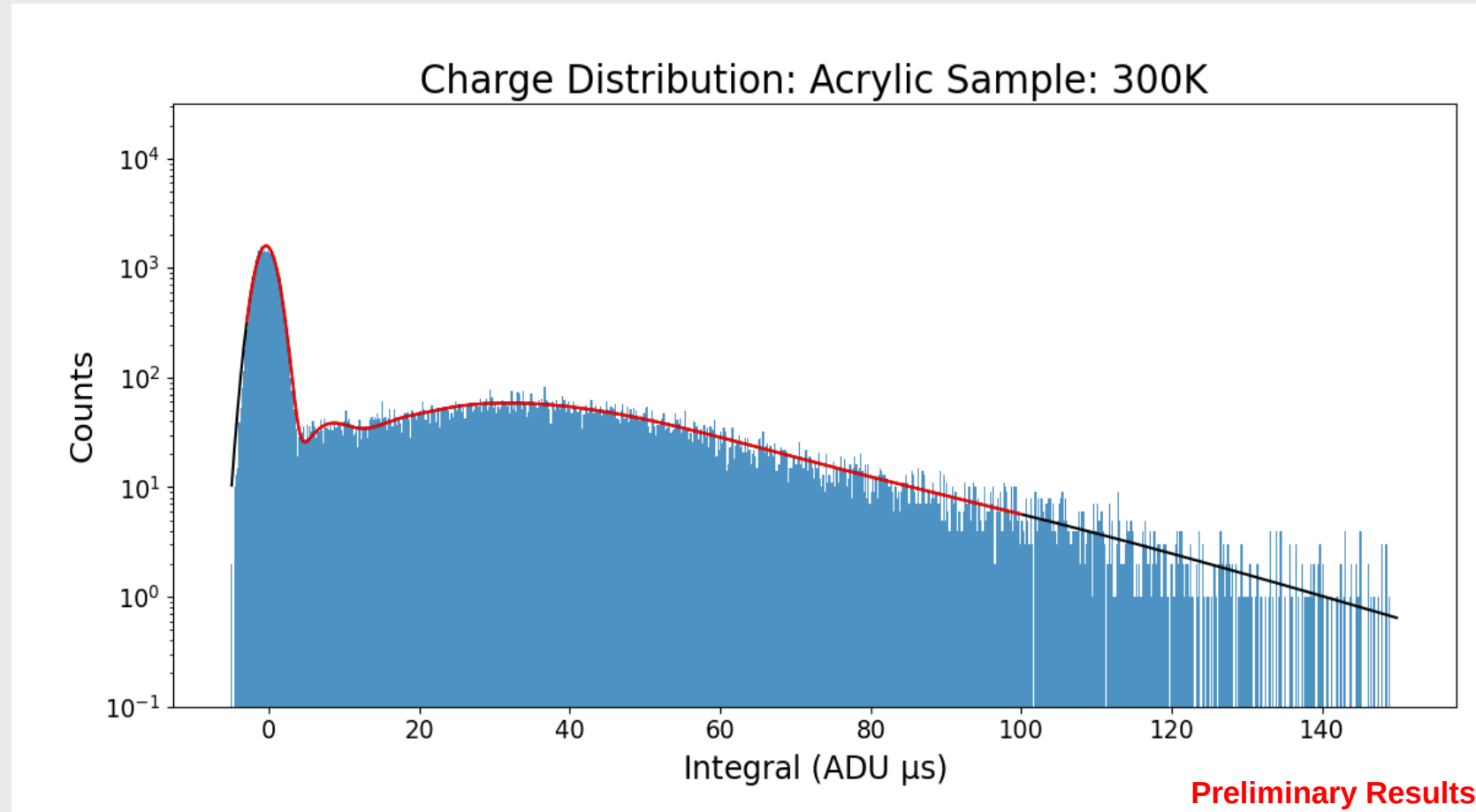
Parameter	Value	Unit
$m$	0.43	PE
$m_1$	0.02	PE
$k$	4.48	1/PE
$x_0$	-0.33	ADU $\mu$ s
$x_1$	8.03	ADU $\mu$ s
$s_0$	1.44	ADU $\mu$ s
$s_1$	2.92	ADU $\mu$ s





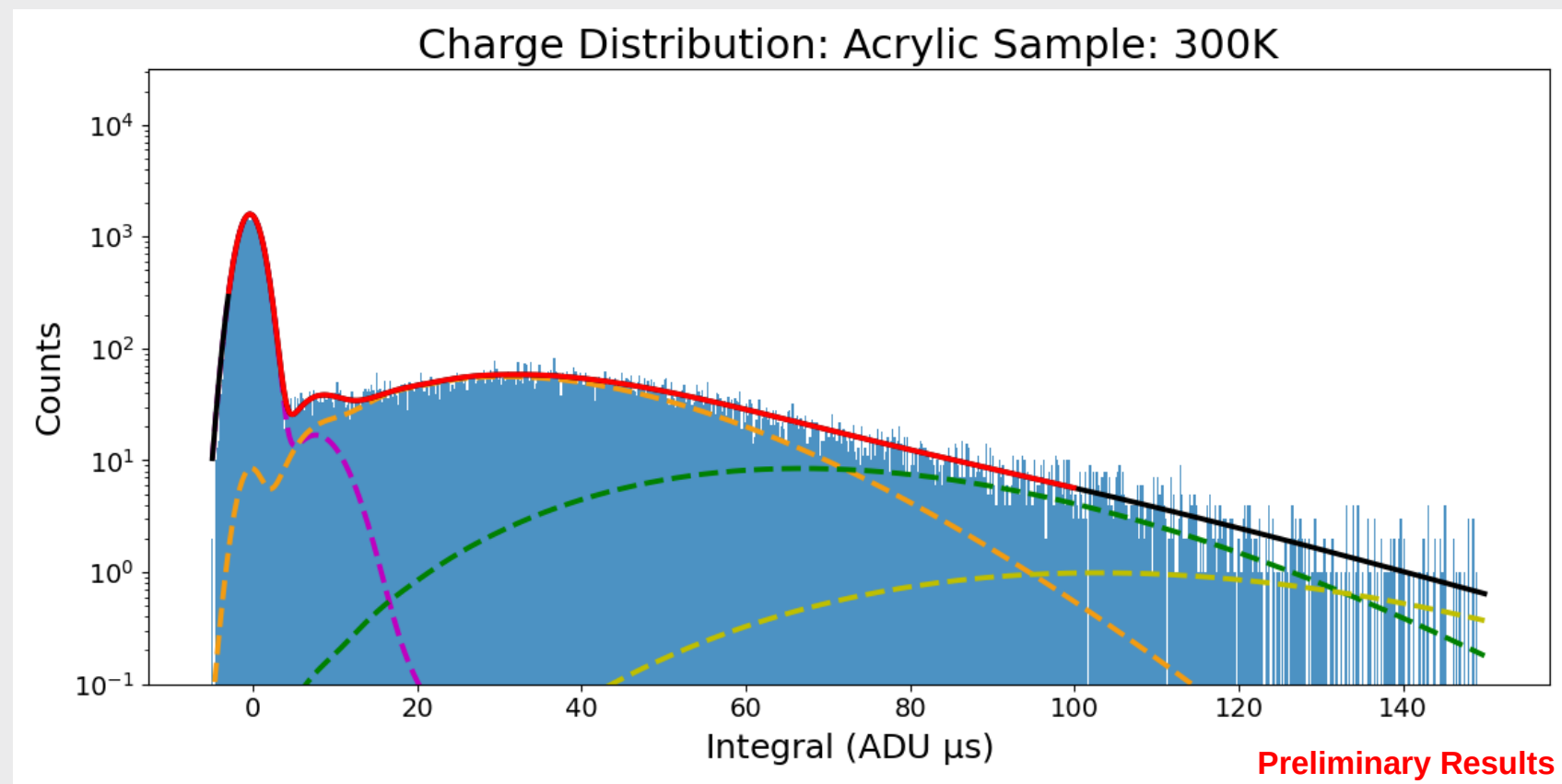
# Individual SPE Data Set: Building the Model

- **Step One: plot the data**
- **Step Two: Determine model parameters by minimization chi2 method and plot the resulting modeled charge distribution.**
- **Step Three: Extrapolate model to larger and smaller charge.**

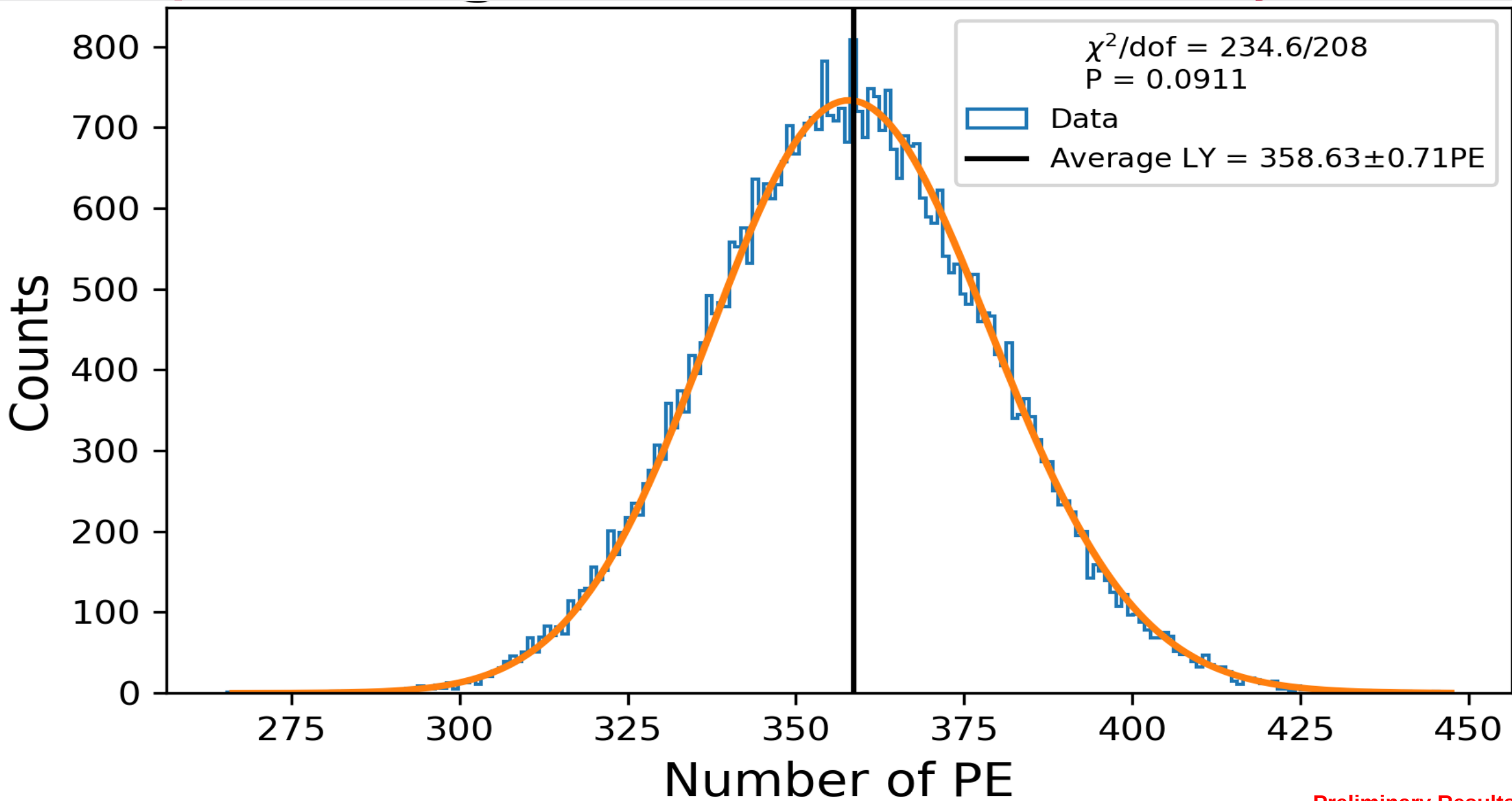


## Individual SPE Data Set: Building the Model

- **Step One: plot the data**
- **Step Two: Determine model parameters by minimization chi2 method and plot the resulting modeled charge distribution.**
- **Step Three: Extrapolate model to larger and smaller charge.**
- **Step Four: Visualize the 0, 1, 2, and 3 PE charge distributions.**

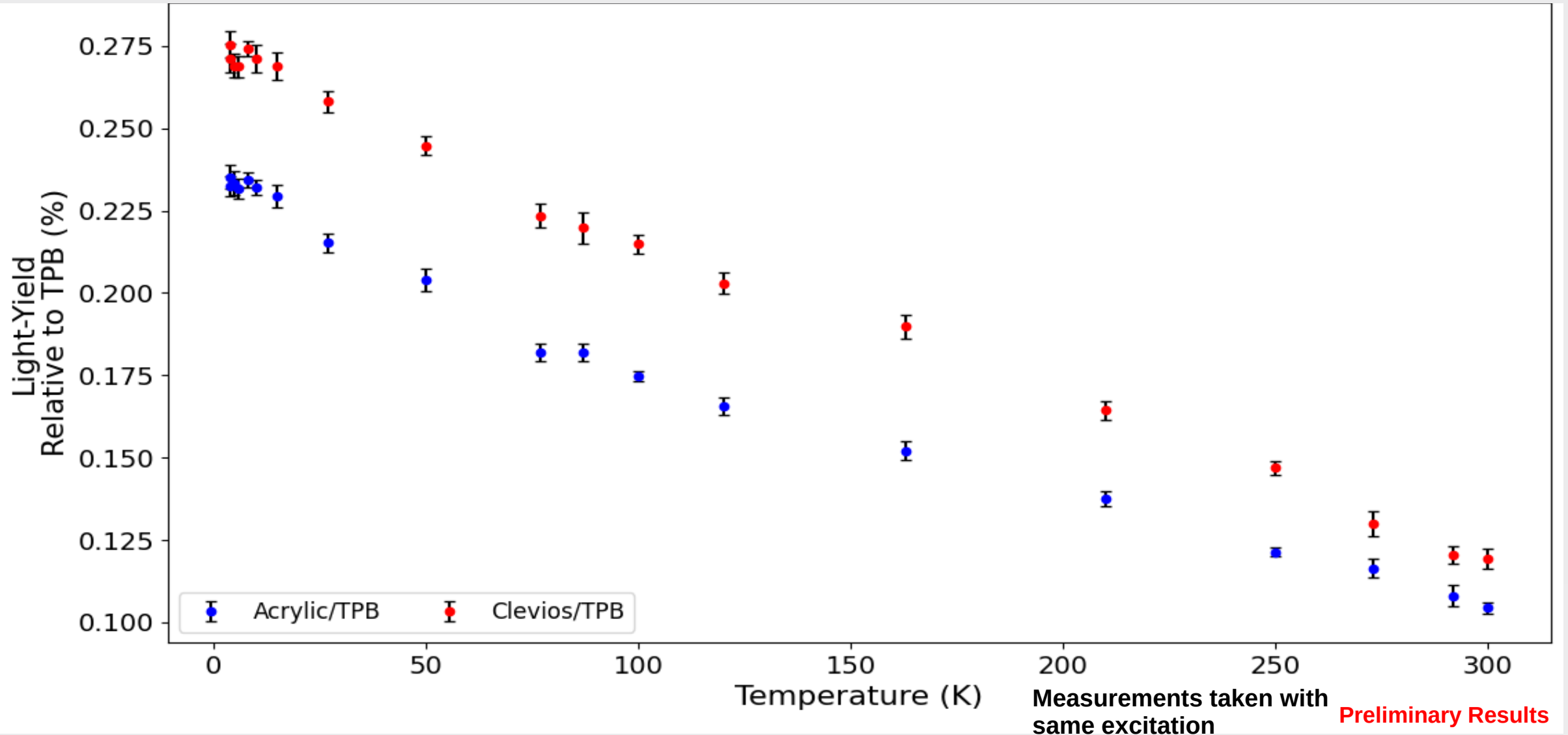


# Multiple Photoelectron Distribution: TPB on Acrylic



## 28 Clevios and Acrylic Light-Yield Relative to TPB

The light-yield of TPB has been heavily studied ([HERE](#), [HERE](#), and [HERE](#)) and has been remeasured for this study. Hence, using the light-yield of TPB as a common reference point to compare the fluorescent intensity of other samples is a useful technique. All measurements taken with **same** excitation.



# Individual SPE Data Set: PMT Model

G(data, mean, Std. Dev.)

$$S_r(\mathbf{x}) = \sum_{n_1, n_2=0}^{10} \sum_{k_1=0}^{120} \frac{m^{n_1} e^{-m}}{n_1!} \frac{m_1^{n_2} e^{-m_1}}{n_2!} \frac{(n_1 \cdot k)^{k_1} e^{-n_1 \cdot k}}{k_1!} G(x, x_0 + (k_1 + n_2) \cdot x_1, s_0^2 + (k_1 + n_2) \cdot s_1^2)$$

Distribution of photoelectrons (PE) generated on the PMT photocathode (PC) window.

$m$  := average number of PE generated on PC.

$n_1$  := actual number of PE generated on PC.

$m$  is referred to as the **average light yield**.

Distribution of photoelectrons (PE) generated on the first dynode of the PMT.

$m_1$  := average number of PE generated on 1<sup>st</sup> dynode.

$n_2$  := actual number of PE generated on 1<sup>st</sup> dynode.

Distribution of secondary electrons generated by first dynode.

$k$  := average number of secondary electrons per primary electron on first dynode.

$k_1$  := actual number of secondaries generated on first dynode.

Gaussian distribution to model noise and charge collected by the anode.

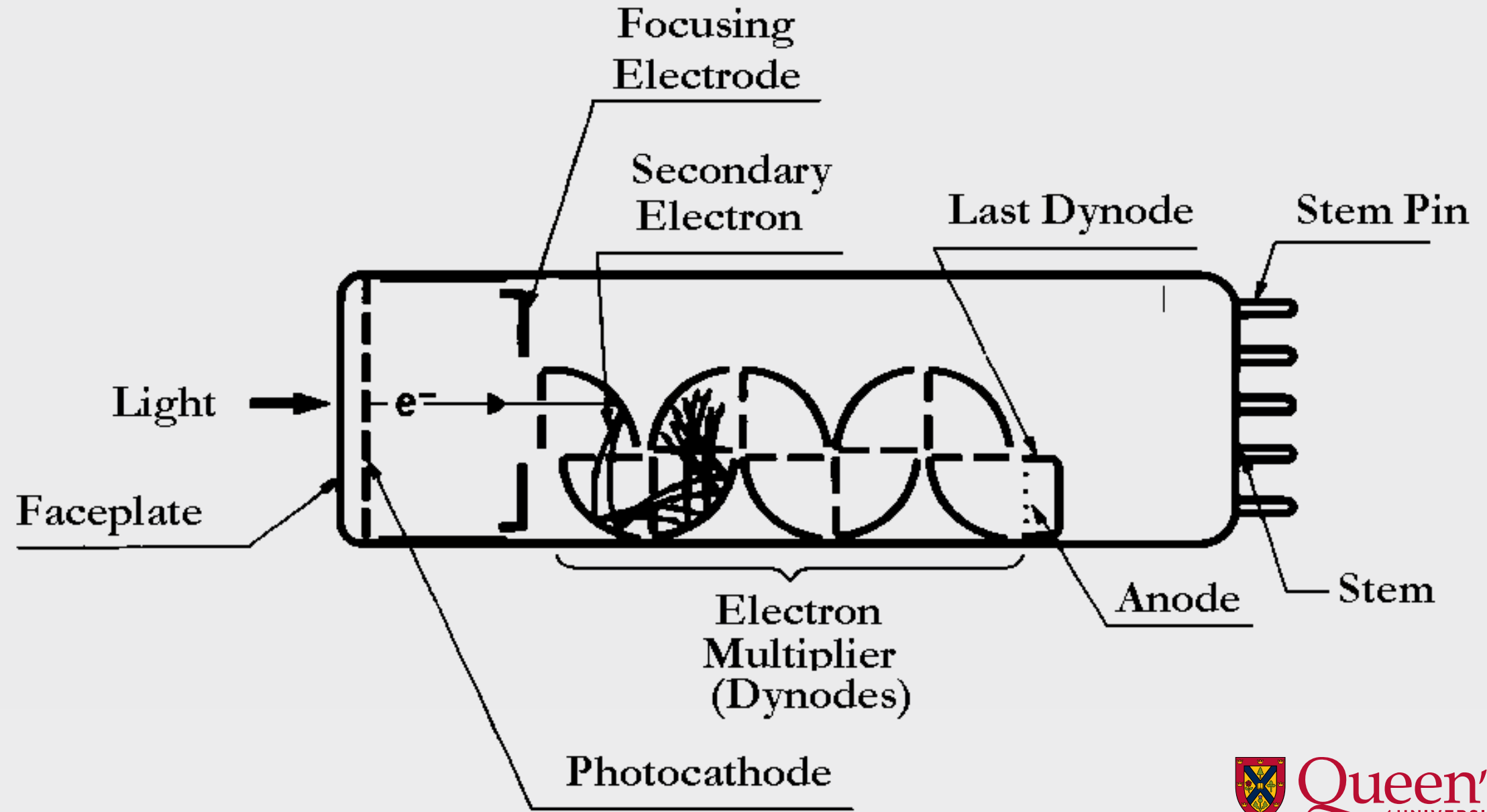
$x_0, s_0$  := average charge collected corresponding to no generated PE, and its standard deviation.

$x_1, s_1$  := average charge collected by PMT anode per electron created on the first dynode, and its standard deviation.

$x$  := counts per bin.

Model can be found in **this** paper: S. Tokar, et al., 1999

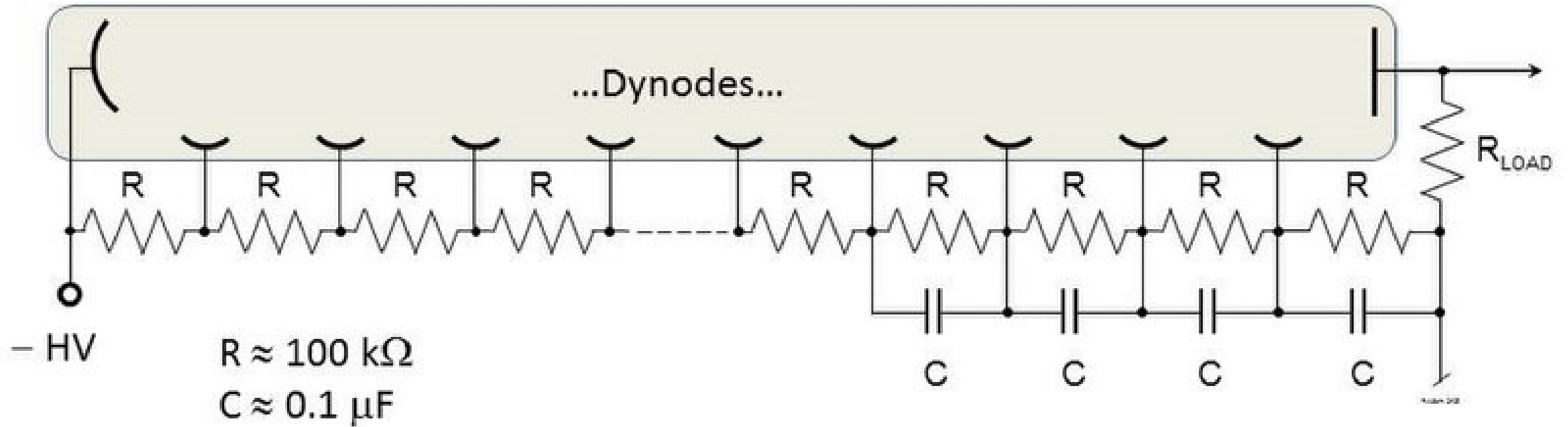
# PMT: Dynode Structure





Photocathode

Anode



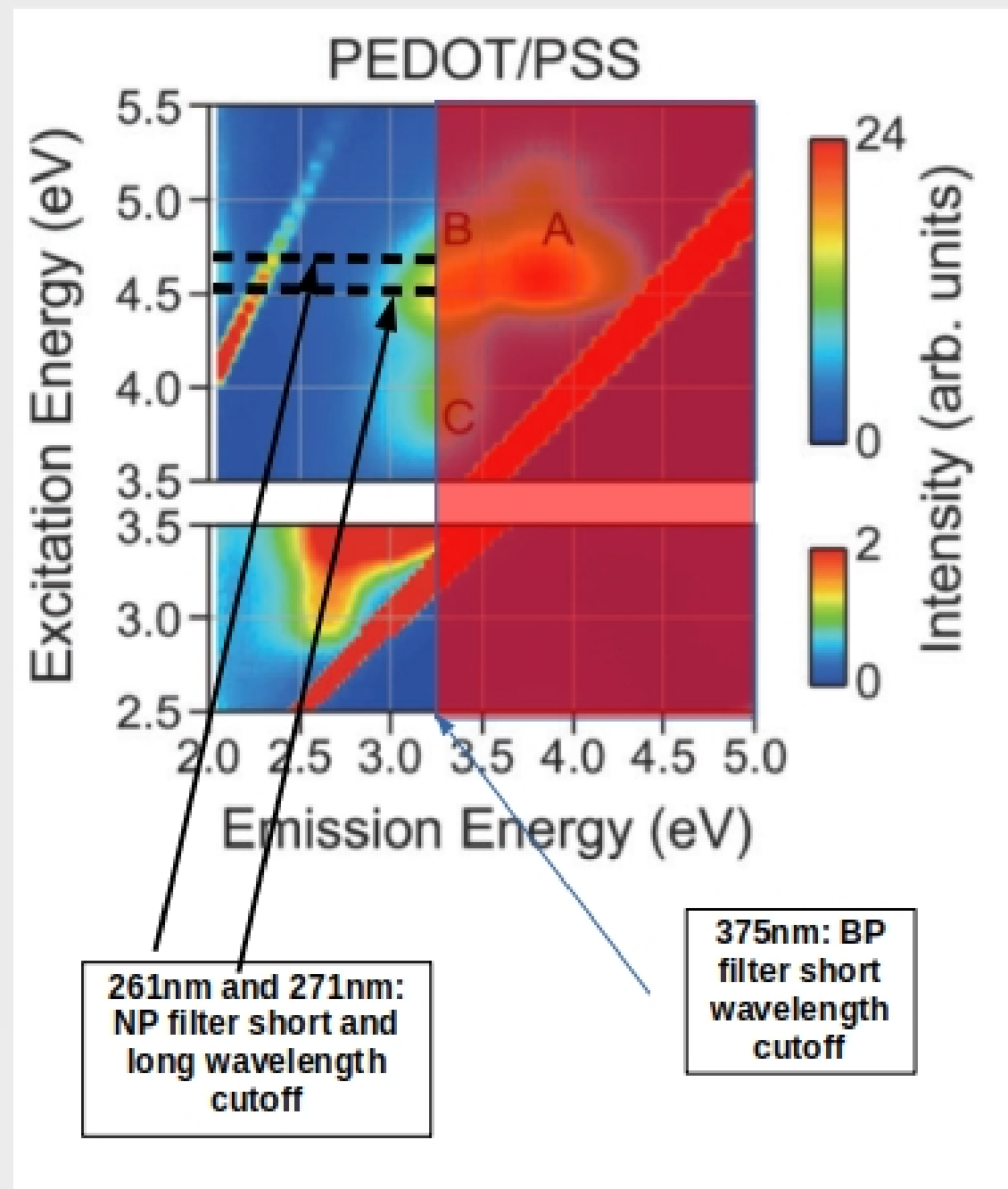
[https://commons.wikimedia.org/wiki/File:PMT\\_Voltage\\_Divider.jpg](https://commons.wikimedia.org/wiki/File:PMT_Voltage_Divider.jpg)



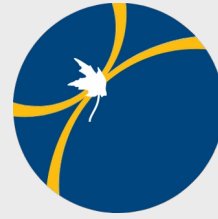
## 32 Why Investigate Clevios?

- Clevios is an organic conductive polymer (sol-gel).
- Main component of Clevios is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)
- Thin coatings of Clevios can be applied to a surface to create a conductive coating.
- There is evidence that PEDOT:PSS exhibits fluorescence upon exposure UV irradiation<sup>1</sup>.
- A study on whether Clevios is fluorescent under UV excitation is key in determining the light contribution Clevios will provide if it is to be used in an experiment such as Darkside that will make use of a time projection chamber (TPC).

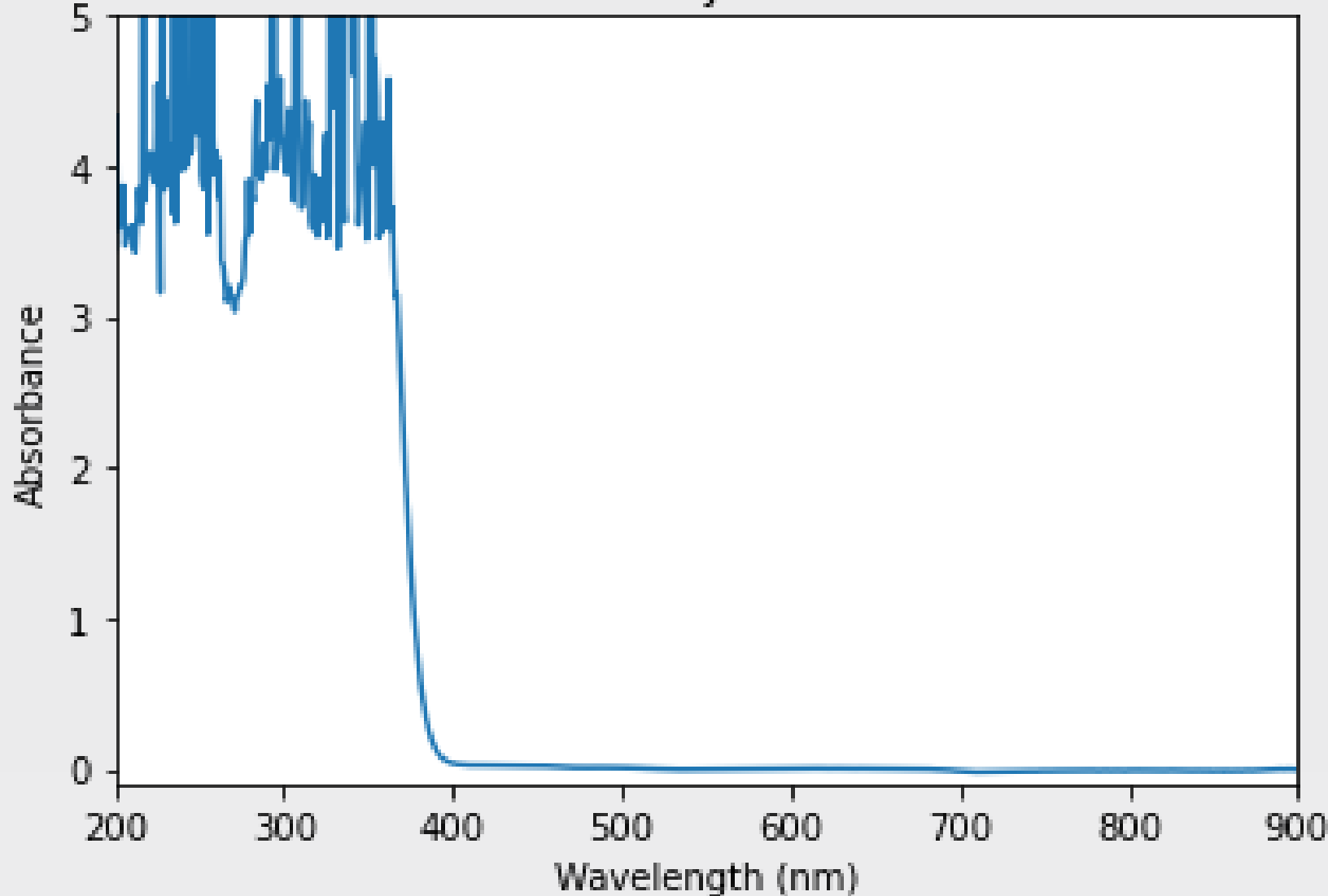
1. T. Koyama et al. Photoluminescence of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in the visible region. J. Mater. Chem. C, 3(32):8307–8310, 2015







Acrylic

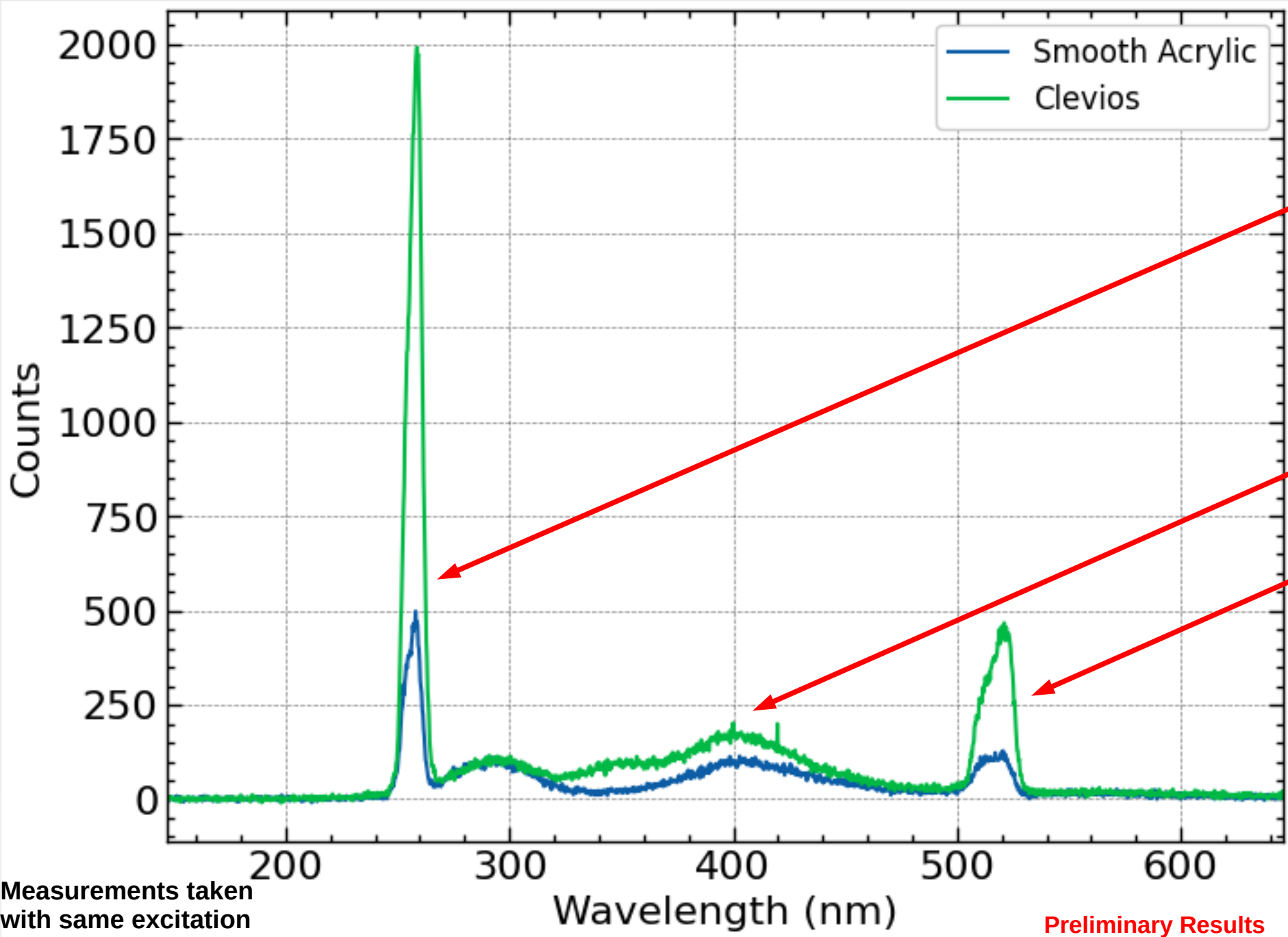


Spectra measured using Cary 60 UV-VIS spectrophotometer provided by Aligent (thanks to the Stamplecoskie group for allowing us to use their set-up!)

Sample irradiated with light produced from Xenon flash lamp.

Wavelengths between 180nm and 900nm are possible to investigate.

Clear absorption below 375nm



260nm LED reflection

420nm acrylic fluorescence

520nm LED Harmonic (spectrometer feature)

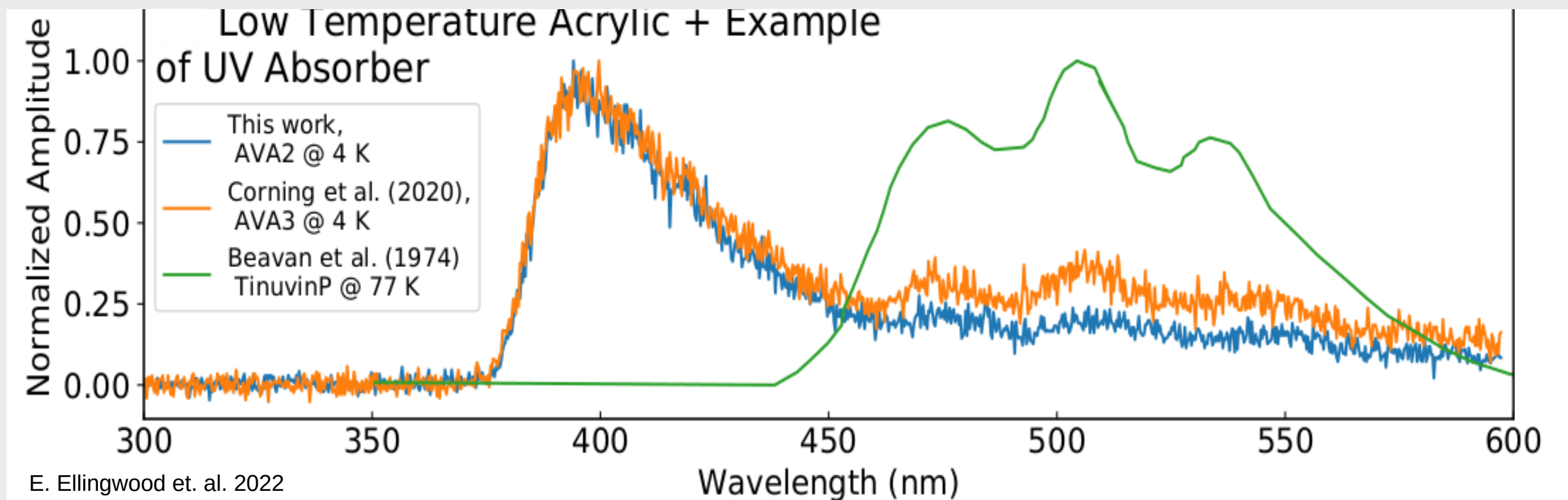
Measurements taken with same excitation

Preliminary Results



## Spectral Measurements: Acrylic Additives

Below: Reported spectral measurements of acrylic upon irradiation by 285nm LED. **Orange** and **blue** curves represent work completed by a previous member of the cryostat team (link [HERE](#)) and our most recent published work (link [HERE](#)). **Green** curve is emission spectrum of a family of compounds including Tinuvin-P (2-(2hydroxyphenyl)benzotriazoles (HBzTs)), a common UV absorbing additive found in acrylic (link [HERE](#)).

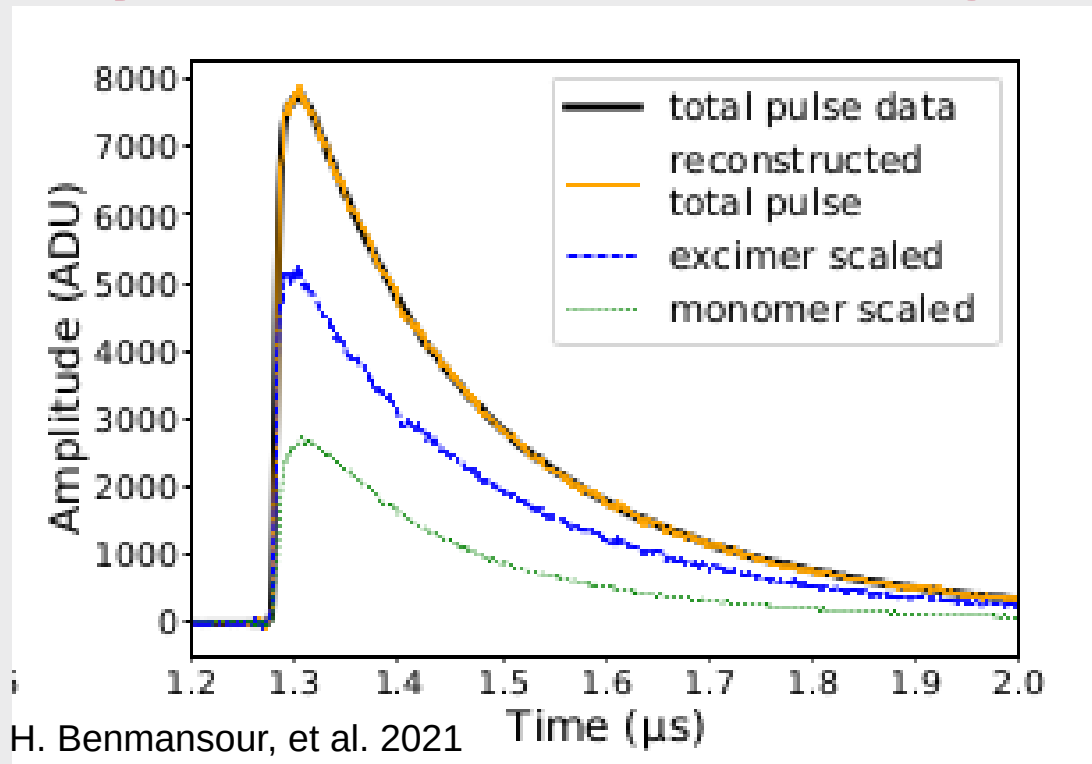


E. Ellingwood et. al. 2022  
J. M. Corning et. al. 2020  
S. Beavan et. al. 1974

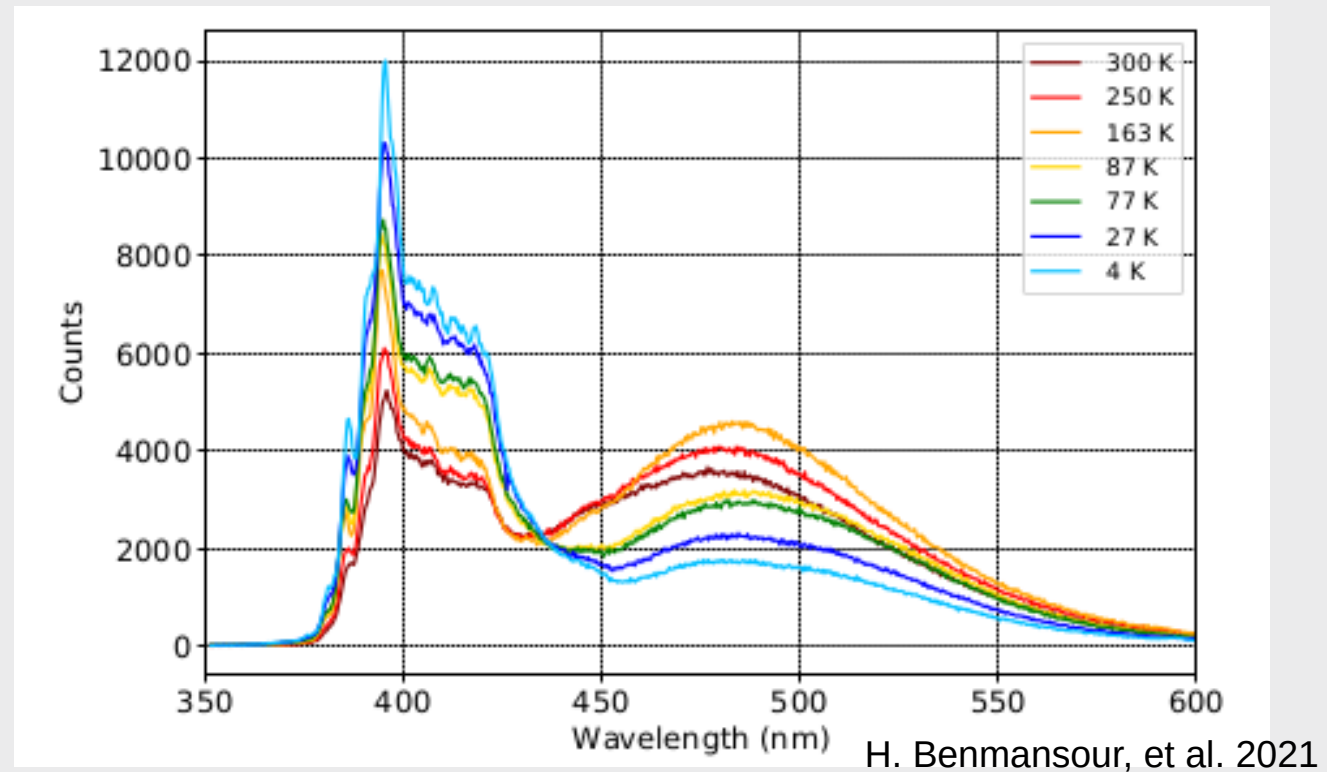


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# 36 Pyrene: Slow Wavelength Shifter



Average waveform from emission of pyrene exposed to 285nm excitation. The total waveform is a convolution of the fast, monomer emission (between 100ns and 125ns) and a slower, excimer emission (between 225ns and 290ns) at 87K.



Pyrene spectrum at various temperatures. These studies were published later 2021 (link [HERE](#)).