Liquid Scintillators

Technology and Challenges

Technology and Instrumentation in Particle Physics (2023) Cape Town, South Africa.

G.G.Stokes (1852) “change of refrangibility of light !”, Born-Oppenheimer approximation (1926) for molecular dynamics, Forster Resonant Energy Transfer (1948) —> Practical metal loaded designed scintillators for neutrino physics (~2000)

Dedicated to Dick Hahn (BNL) rest in peace: 2022.

Milind V. Diwan September 7, 2023 (updated)

Thanks to many colleagues for slides and reviews: Minfang Yeh provided much of the data in this presentation.

Stokes: Although the passage through a thickness of fluid amounting to a small fraction of an inch is sufficient to purge the incident light from those rays which are capable of producing epipolic dispersion, the dispersed rays themselves traverse many inches of the fluid with perfect freedom. It appears therefore that the rays producing dispersion are in some way or other of a different nature from the dispersed rays produce.

In an astonishing paper of 100 pages, Stokes shows that the nature of light is independent of its origin, and that upon what he calls “dispersion” in materials the invisible rays (ultraviolet) shift to rays of visible light that have lower “refrangibility” meaning index of refraction. He even remarks that this effect is particularly common in organic liquids.

Understanding ionization in materials

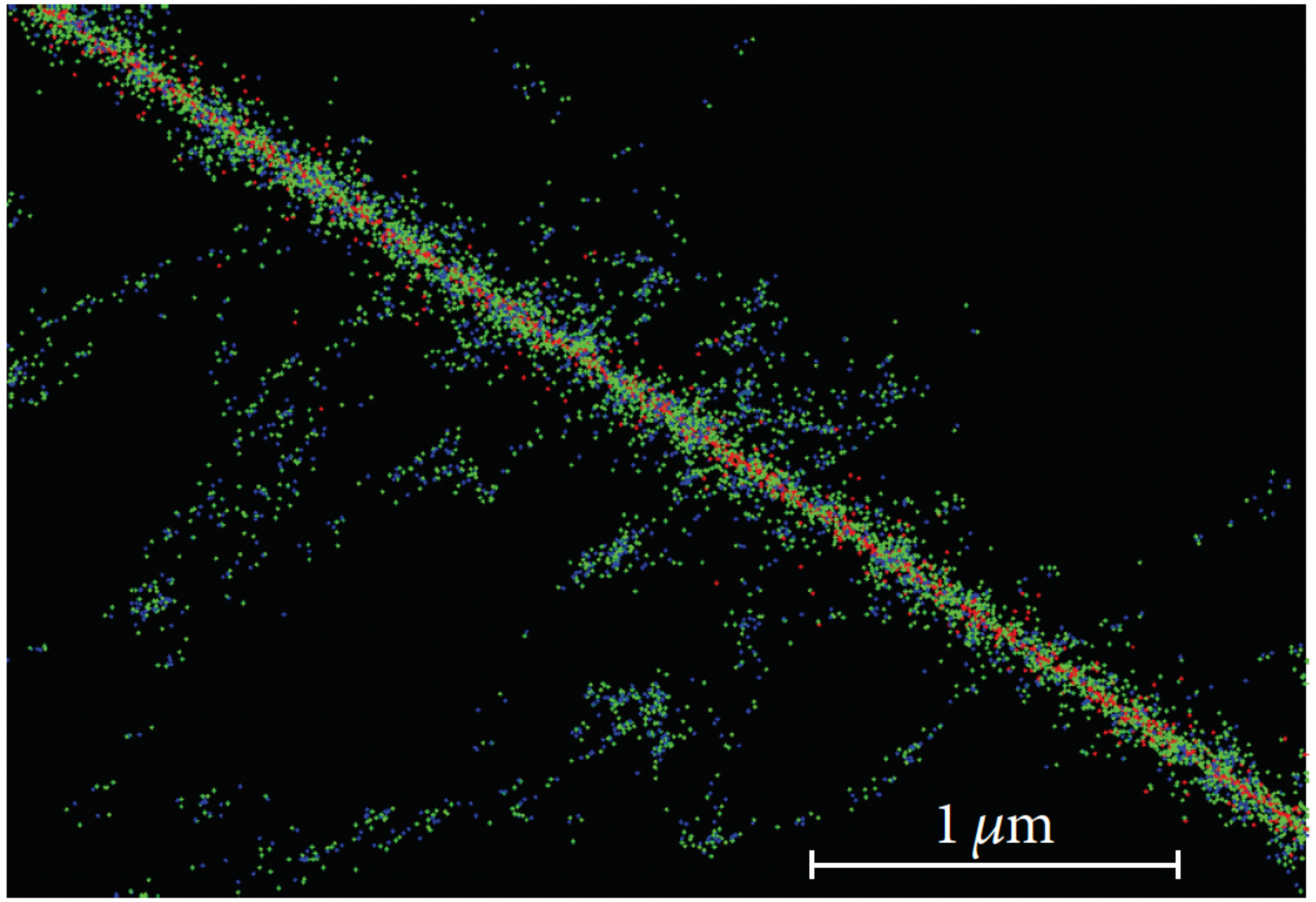


FIGURE 1: The track structure of a single proton in water. Simulated using RITRACKS. Red: proton ionisation, green: electron ionisation, and blue: hydroxyl radicals.

Detailed understanding of cross sections and molecular states in liquid is needed for this level of simulation. Geant-DNA and RITRACKS are codes developed to specifically understand water ionization.

It would be a great challenge to perform this kind of simulation for organic scintillators as well as noble liquids.

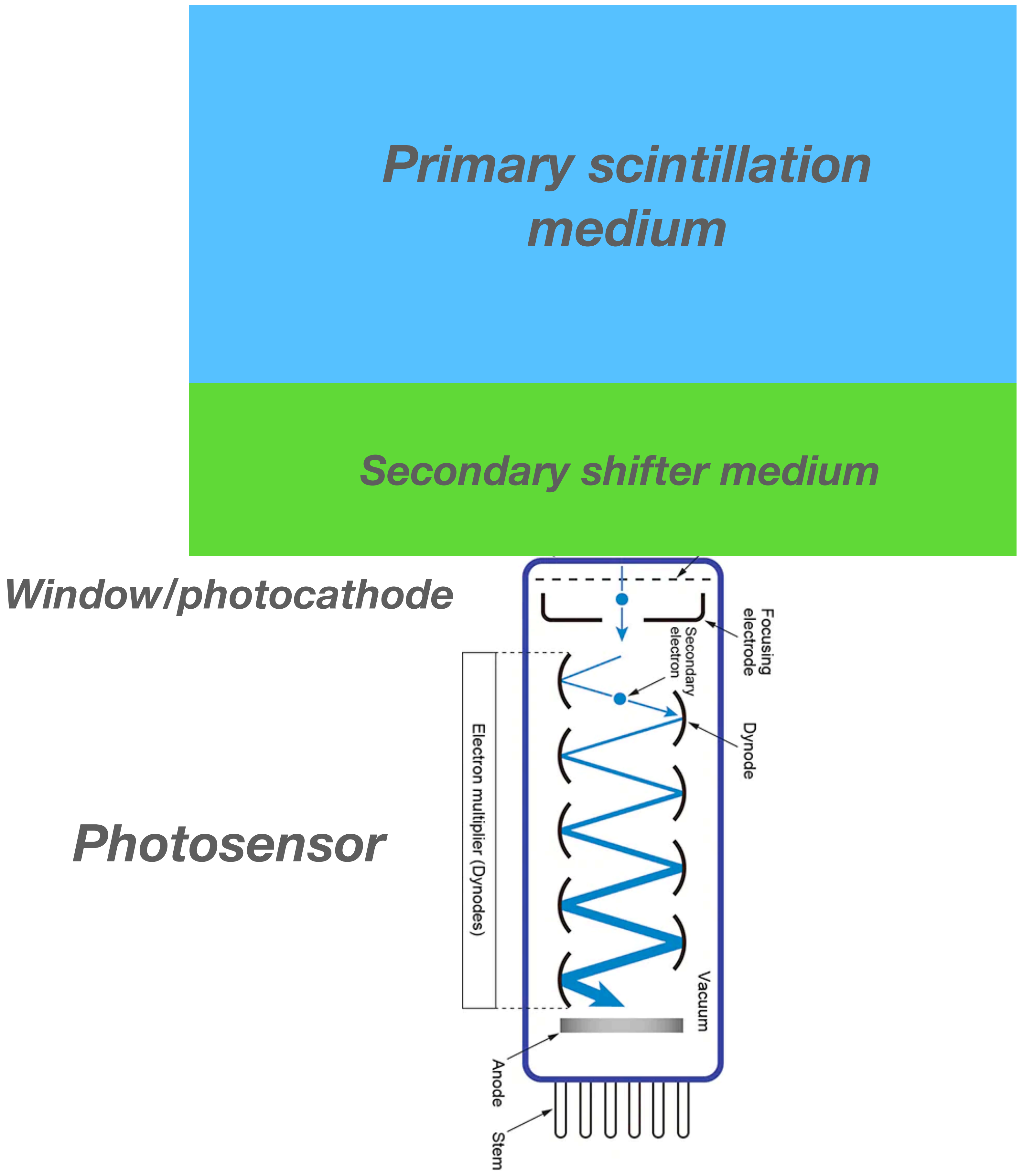
Reference: Douglas, Penfold, Bezak, Computational and Mathematical Methods in Medicine, June 2015

Also see H. Bichsel (2006) on corrections to dE/dx for atomic effects.

Outline of talk

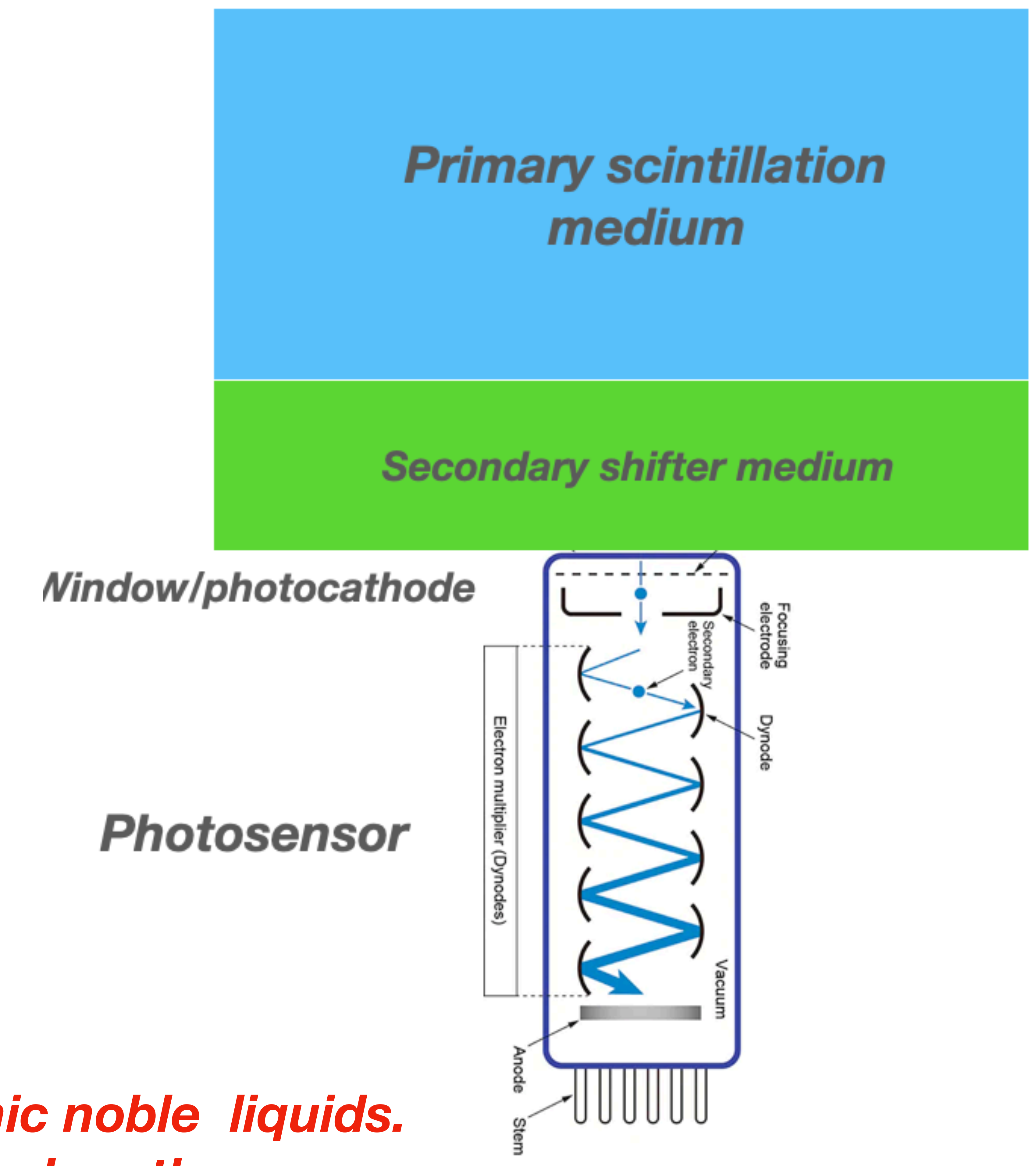
The practice of liquid scintillators, organic and noble liquids, status and future.

- *Introduction to liquid scintillators*
    - *General detector considerations*
    - *Fundamentals for organic versus noble liquids.*
    - *Production and detection considerations.*
- *Organic liquid scintillators*
    - *Example usage*
    - *Current typical performance.*
    - *Future developments in Cherenkov and scintillation combination: tuned metal loaded and water based liquid scintillators*
- *Noble liquid scintillators*
    - *Contrast noble liquids with organic scintillators.*
    - *Current typical performance (ICARUS and DUNE detectors)*
    - *wavelength shifters and readout*
- *Summary and future directions.*
    - *Future engineering of coupled scintillation and optical systems*
    - *Future of simulations and calibration.*



Practical detector considerations

- Detectors must operate under achievable conditions: either STP or cryogenic with reasonable pressures.
- Wavelengths must match available detectors and practical optical windows. Very difficult under 200-300 nm.
  - work is in progress to us VUV SiPM’s in liquid argon.
- Detector size and attenuation of the light must have good match. Materials must not absorb own emission.
- Signal to noise in detectors: need to achieve enough current in detectors to get ~1 volt signal after amplification.
  - This limits the choices to photomultiplier tubes or modern SiPMs (at low temperatures).
- Cost needs to be kept reasonable.
- Safety: toxicity, material compatibility, oxygen deficiency hazard, flash point must be considered.



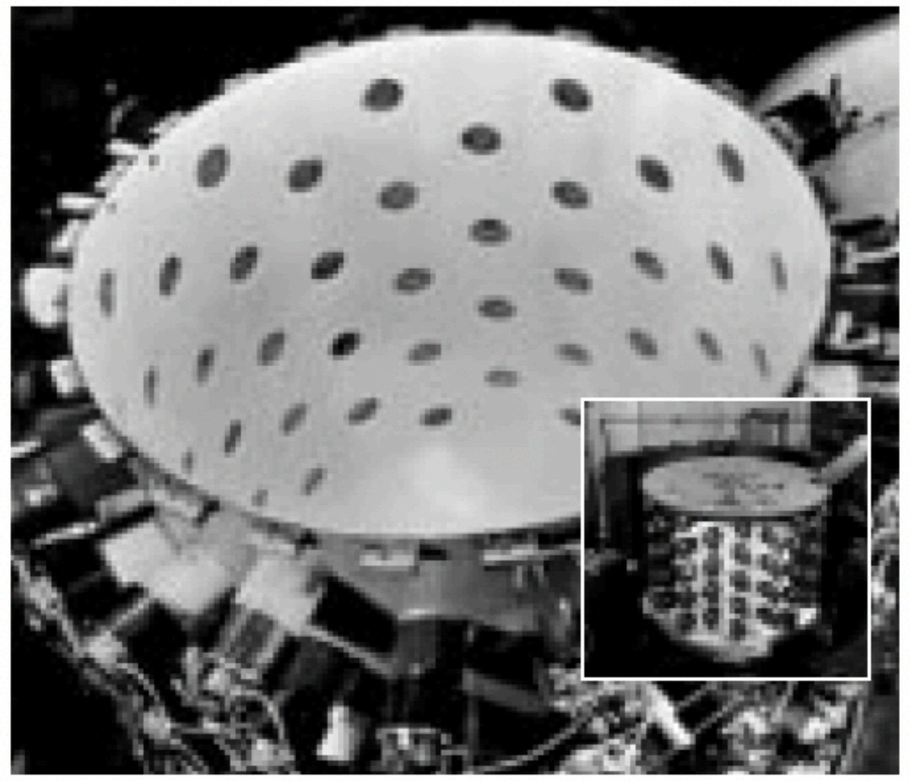
Practical Conditions limit us to ~200-600 nm, and to organic or cryogenic noble liquids.
For liquid Xenon, quart windows are used to reach lower in wavelength.

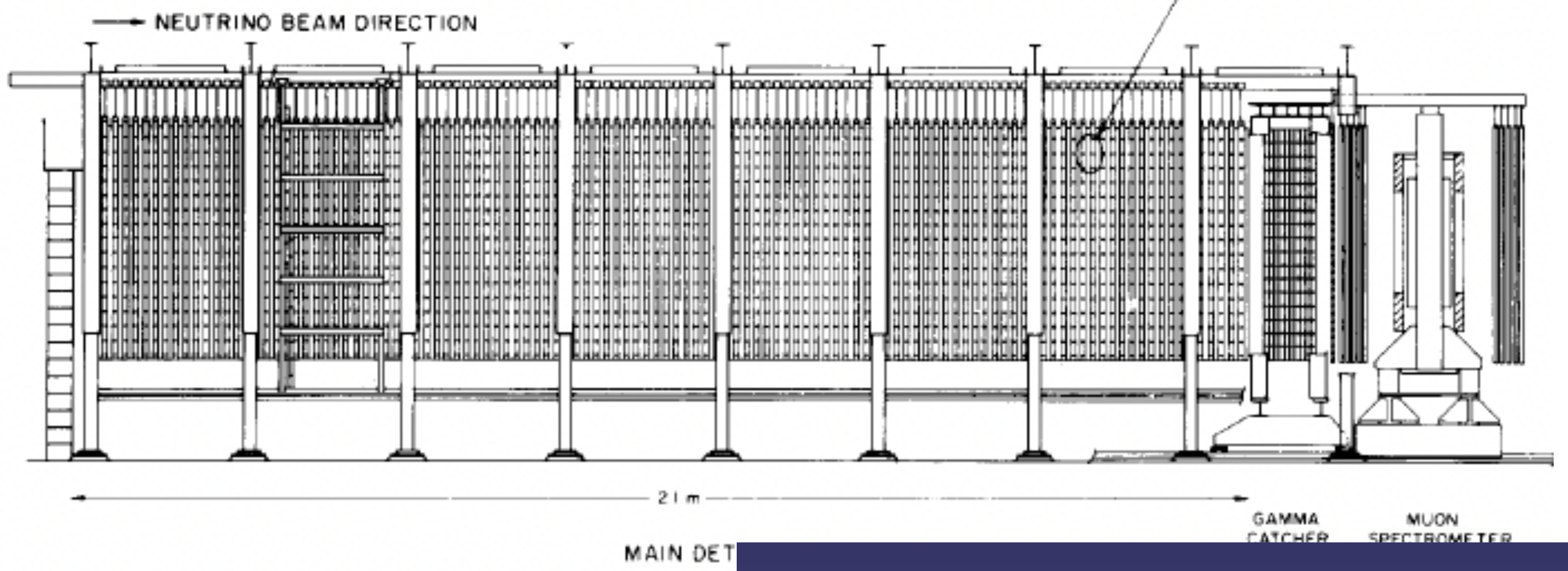
Advantages and History

The advantages have allowed many discoveries, especially in neutrino physics.

Reins and Cowan (Herr Auge 300 lt detector) (Cd loaded) Los Alamos Science, No. 25, 1997

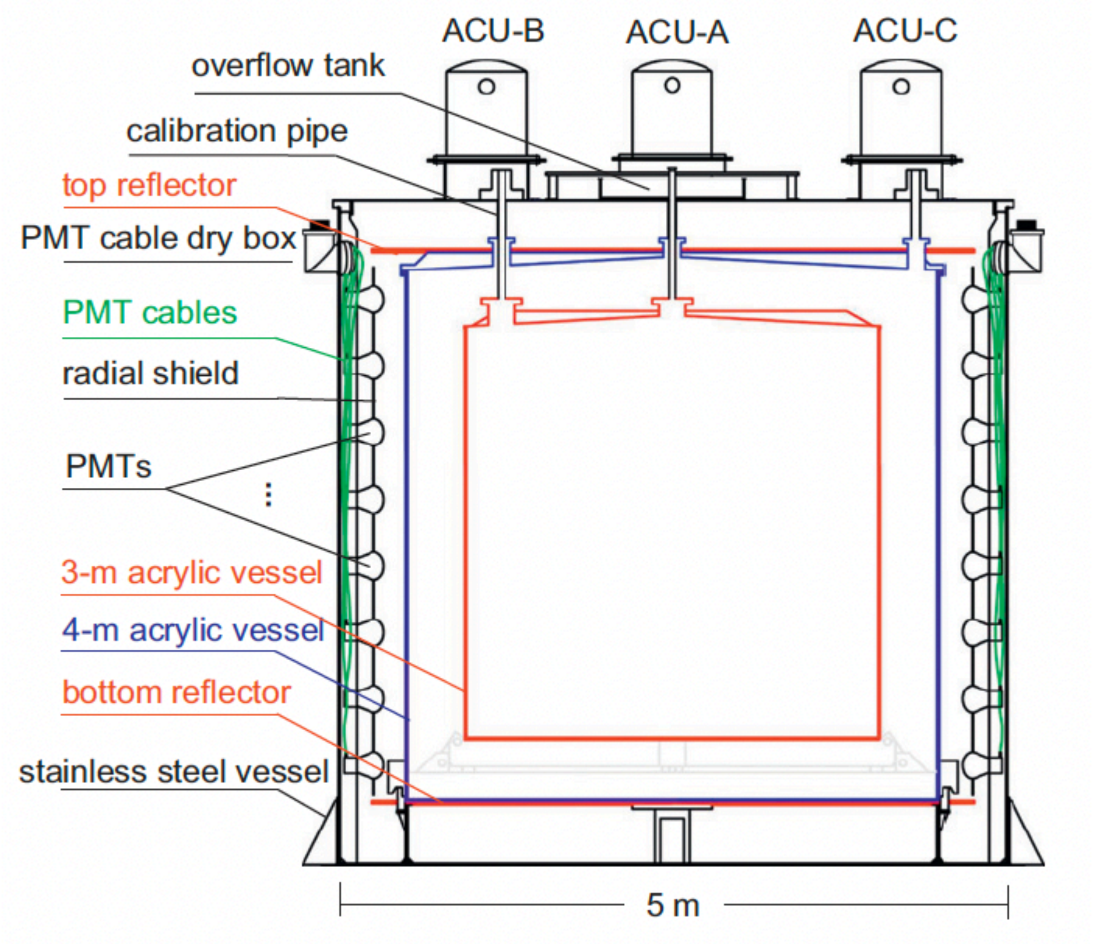
First metal loaded large LS detector at Hanford. (1953)





BNL-E734 170 tons

NIM A254 (1987) 515



Daya Bay (20 ton fid, 8 modules)

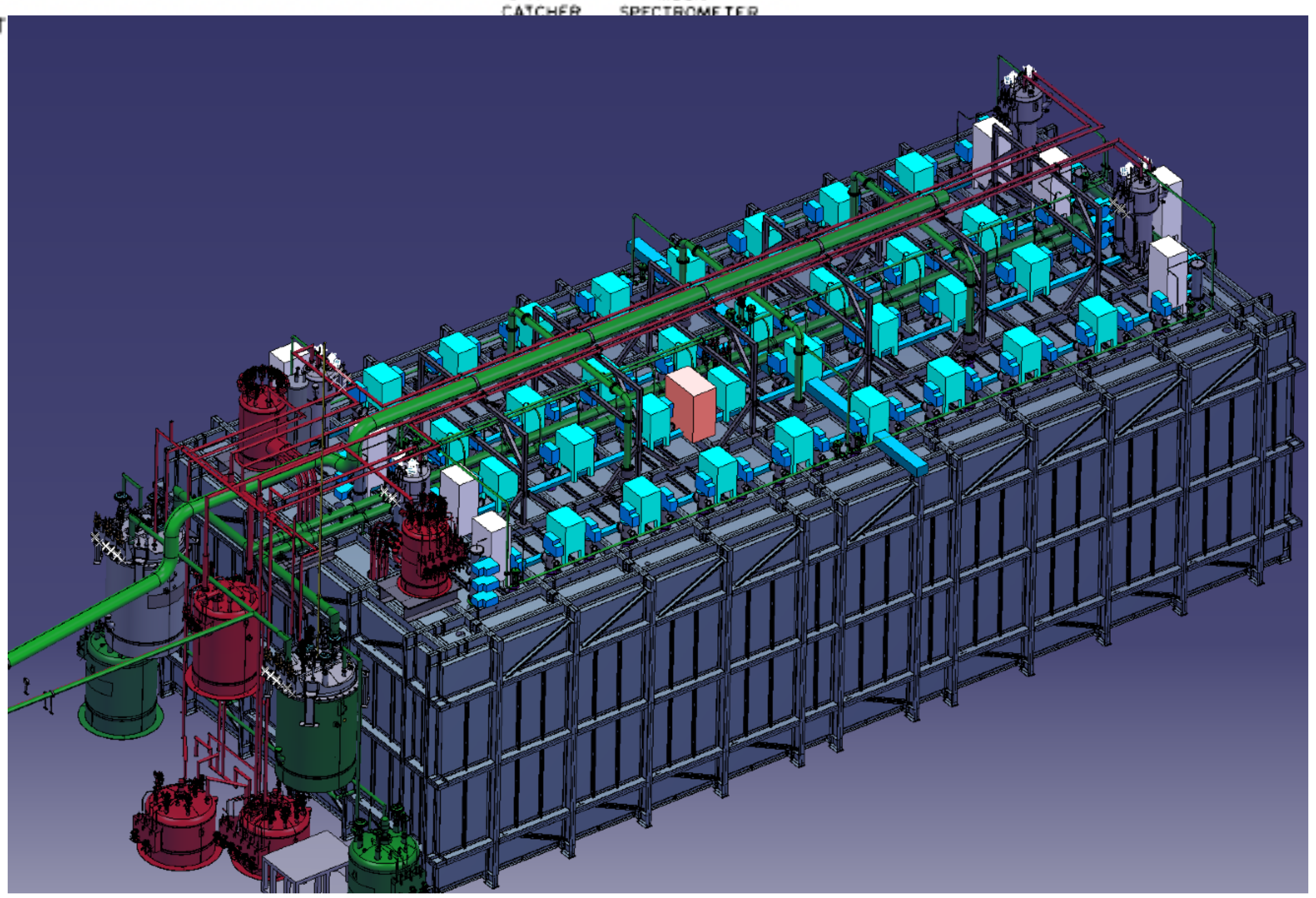
(Gd loaded for reactor IBD detection)

NIM A685 (2012) 78-97

ICARUS T600 at Fermilab in two 300 ton liquid argon modules.

The cryogenic systems are shown. Magenta are electronics locations

2022

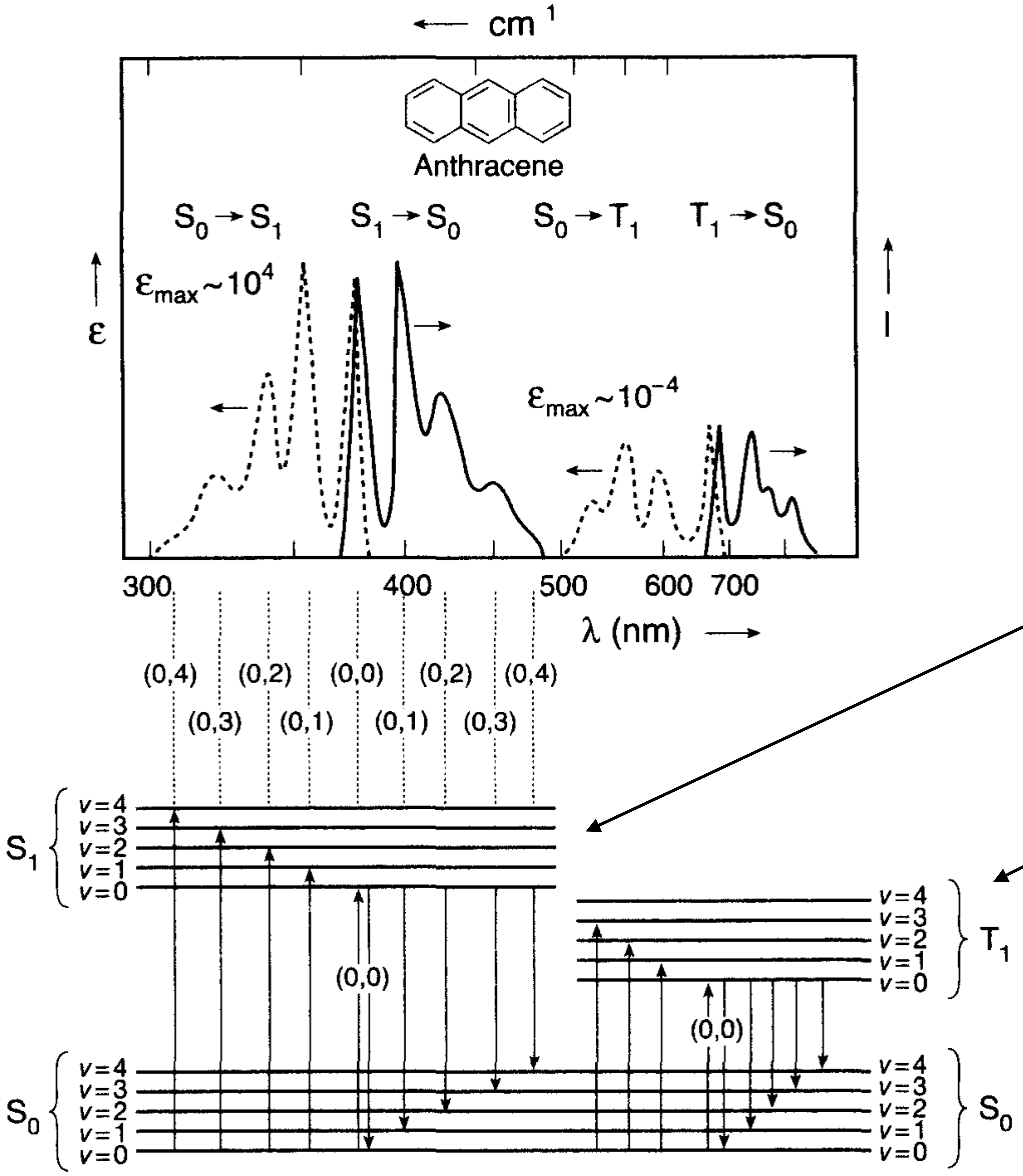


Advantages of liquid scintillators: materials can be found to have high light yield, fast timing, PSD, and compatibility with reasonable containers windows. Liquids also provide the possibility of loading with metals or other functional atoms/molecules in a practical way.

Please look for talks from KamLand, SNO+, and JUNO. These are monumental detectors with extraordinary contributions. LS detector review will be by Guafu Cao on Friday. Josh Klein will provide a review of large Cherenkov detectors.

Jablonski diagram

The key reason scintillators work is because of the Stokes shift. Or the separation between the absorption and the emission wavelengths.



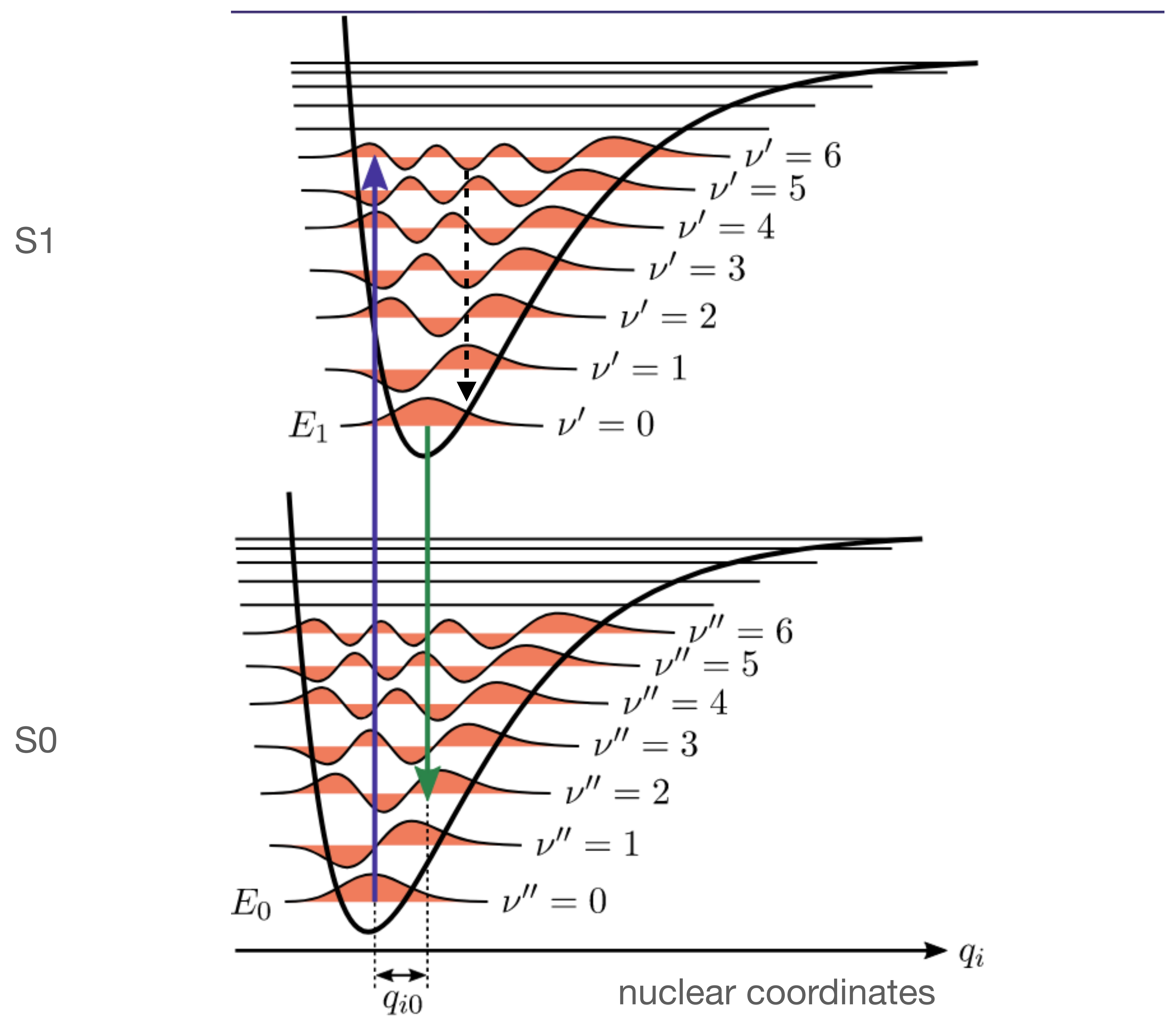
Nicholas J. Turro, Principles of Molecular Photochemistry

- Born and Oppenheimer created an approximation to explain molecular energy levels.
- The molecular wave function can be separated into (1) electronic(S, T, etc), (2) molecular vibrational, and (3) rotational pieces and computed separately. $\psi_e \times \psi_v \times \psi_R$
- The vibrational wave function is computed in a potential defined by the electronic wave function.
  - e.g. Harmonic potential leads to equally spaced energy levels.
- The main singlet states form a series of states $(S_{0n}, S_{1n}, S_{2n} \ldots)$. A spin flip of an electron (spin orbit coupling) causes triplet states with slightly lower energy $(T_{1n}, T_{2n}, T_{3n} \ldots)$.
- Triplet to singlet transitions are forbidden to first order and so they have long livetimes.
- Vast literature to understand the transitions, and potential.
- See chapter III from Arno Bohm (1979) for basics.

Also see detailed lecture from Prof. Ken Hanson (FSU)

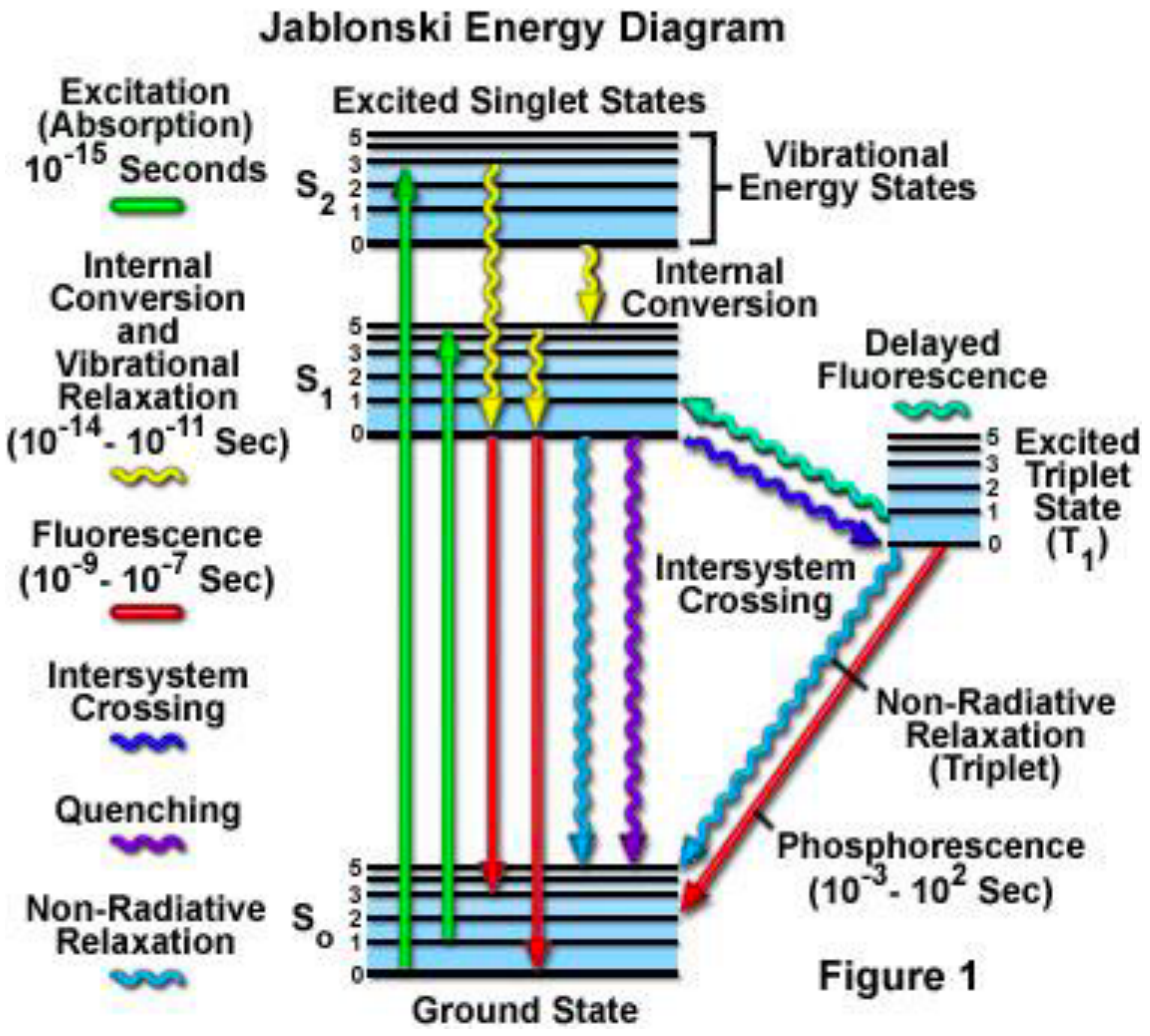
Franck-Condon principle.

Transitions must follow rules that create the Stokes shift.
So that the material does not absorb its own emission.



- The vibrational wave functions in nuclear coordinates are parametric with respect to the electronic wave functions.
- The electronic transitions happen much faster than the nuclear motions.
- The vibrational wave functions must have strong overlap for the transition to take place.
- If an unexcited molecule is S_{00} then it can only go to some S_{1n} state => absorption of shorter wavelength photons.
- An excited state relaxes non-radiatively quickly through vibrational modes to come to S_{10} and therefore emission of longer wavelengths is favored.
- Details depend on the molecule also its environment such as the liquid state.

Picture for a typical organic



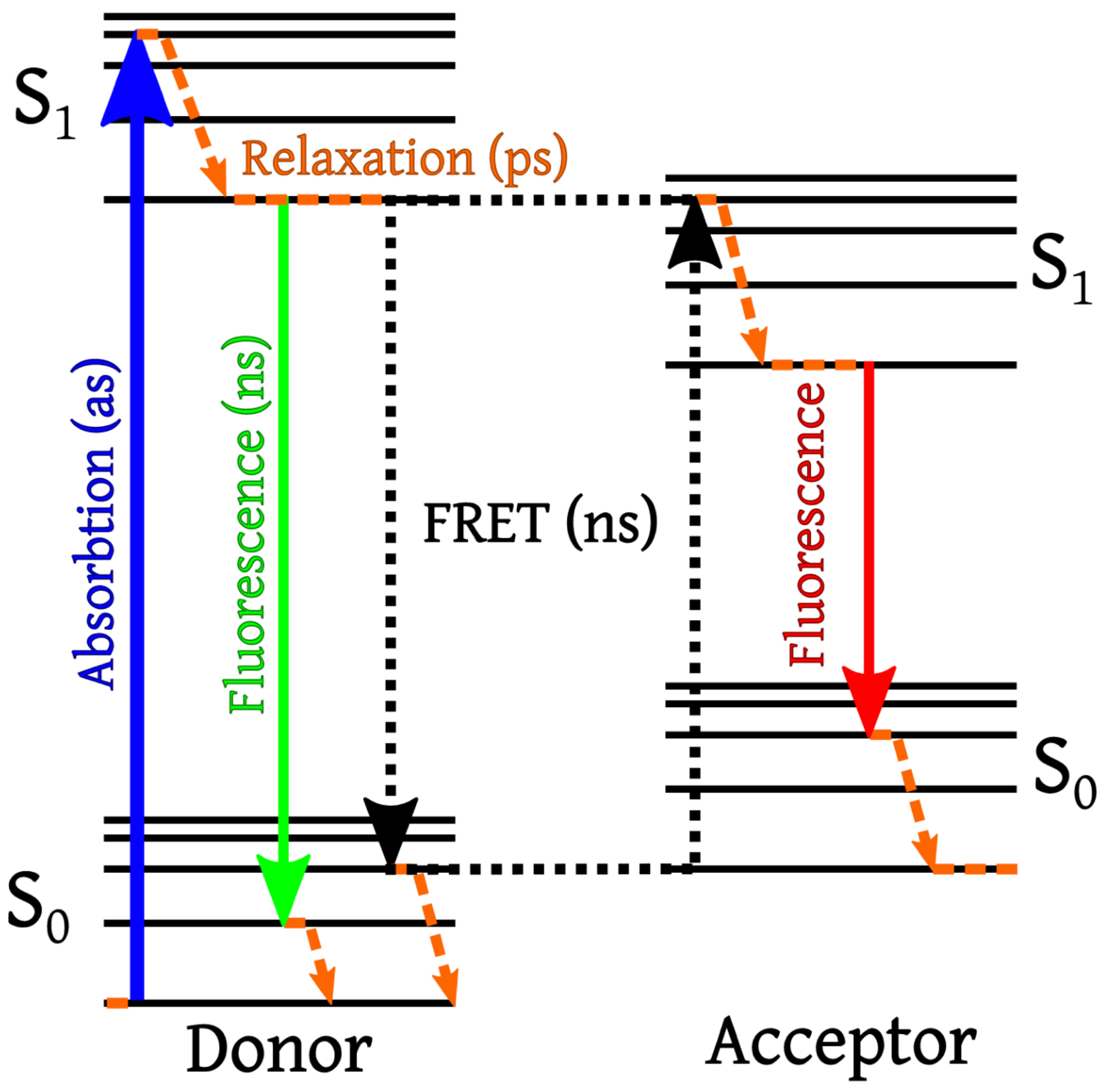
- Ionization excitation is very fast: fsec
- Heavy ionization would populate T_1 states preferentially.
- Non-radiative transitions from S_{1n} to S_{10} are fast (ps)
- Radiative decay from S_{10} to S_{0n} governs the main scintillation timing (ns)
- Non-radiative decays cause quenching (or release of energy without emission)
- T_1 to S_0 is forbidden by parity. And so this can cause long time tails to the emission. This is always present, but wavelength could vary.

Summary: ***all absorption is from the bottom S00 state. And all emission is from either S10 or T10 states. This creates the reflected pattern of absorption and and emission.***

http://micro.magnet.fsu.edu/primer/techniques/fluorescence/fluorescenceintro.html

The Forster Resonant Energy Transfer (FRET)

This it the final piece that allows engineering of the scintillation materials.

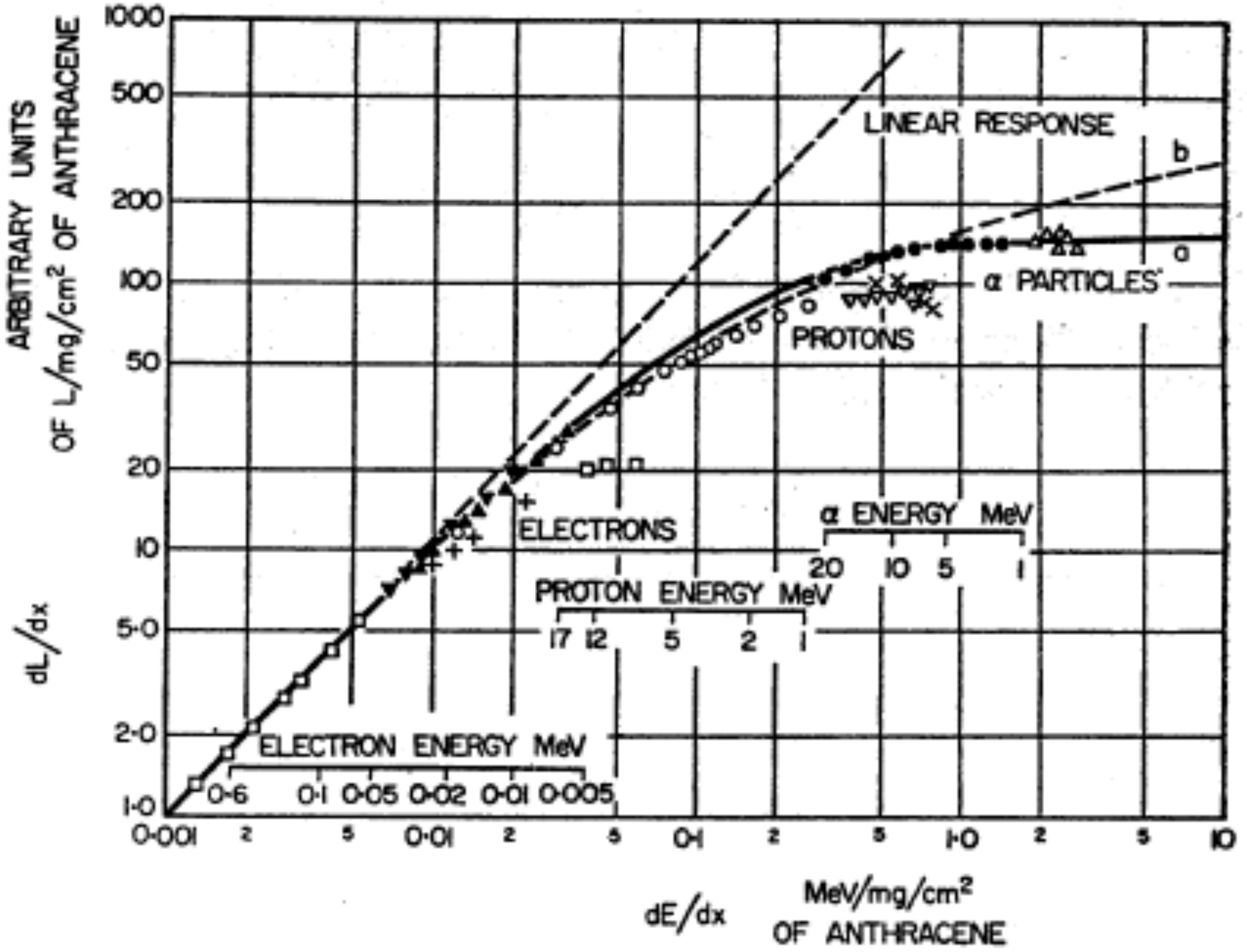


Wikipedia

- Quantum Yield low for most solvents. Absorption and emission spectra overlap.
- A secondary or tertiary fluor needed to shift the wavelength for long attenuation length.
- FRET enables energy to be transferred nonradiatively from solvent to shifter (dipole-dipole interaction (dashed)).
- Efficiency ~ $(1 + (r/R_0)^6)^{-1}$ is very sensitive to intramolecular distance (1-10nm)
- R_0 depends on the QY of the donor, and the spectral overlap of the donor and acceptor.

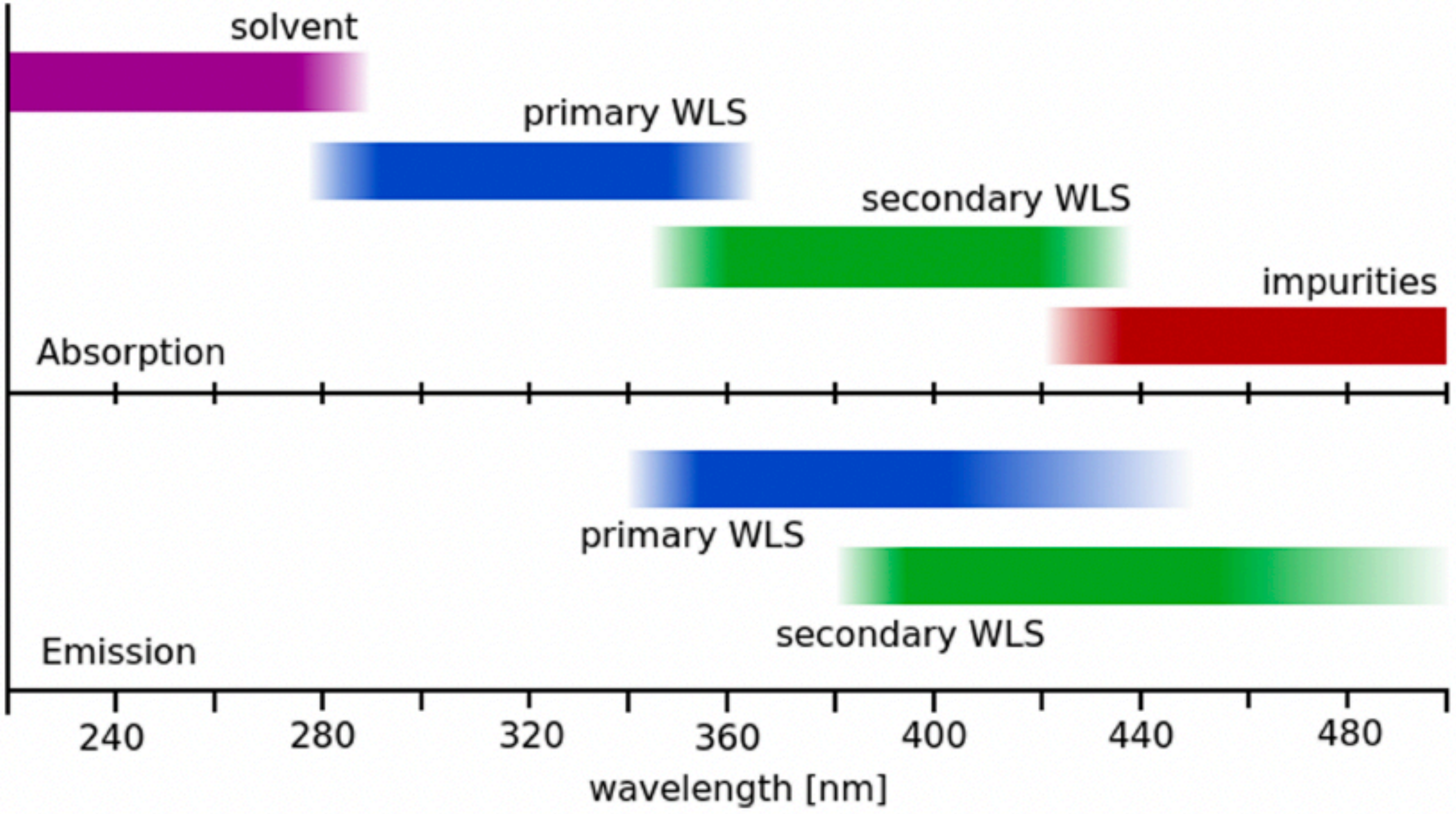
Quenching

From Birks (1964)



- Many ways to lose light so that the yield is not what is expected or linear with ionization energy loss.
- At high ionization densities energy can be lost non-radiatively.
- In particular, it can be lost to the triplet state.
- Birks approximate formula is useful when corrections are small.
- $\frac{dL}{dx} = \frac{L_0 \frac{dE}{dx}}{1 + kB \frac{dE}{dx}}$ where kB is a constant dependent on material and particle type.

Overall picture



Actual spectra in practice in liquids can shift and distort upto 10 nm due to bulk effects. Impurities can cause scattering or absorption.

Common organic solvents and fluors

Table 1. Density, flash point and the wavelengths of the optical absorption/emission peaks (dissolved in cyclohexane) for several solvent candidates are shown.

Molecule	Chemical formula	Density ($kg\,l^{-1}$)	Flash point	abs. max.	em. max.
PC	C_9H_{12}	0.88	48 °C	267 nm	290 nm
toluene	C_7H_8	0.87	4 °C	262 nm	290 nm
Anisole	C_7H_8O	0.99	43 °C	271 nm	293 nm
LAB	—	0.87	~140 °C	260 nm	284 nm
DIN	$C_{16}H_{20}$	0.96	>140 °C	279 nm	338 nm
o-PXE	$C_{16}H_{18}$	0.99	167 °C	269 nm	290 nm
n-dodecane	$C_{12}H_{26}$	0.75	71 °C	—	—
Mineral oil	—	0.82–0.88	>130 °C	—	—

Molecule	Chemical formula	abs. max.	em. max.
PPO	$C_{15}H_{11}NO$	303 nm	358 nm
PBD	$C_{20}H_{14}N_2O$	302 nm	358 nm
butyl-PBD	$C_{24}H_{22}N_2O$	302 nm	361 nm
BPO	$C_{21}H_{15}NO$	320 nm	384 nm
p-TP	$C_{18}H_{14}$	276 nm	338 nm
TBP	$C_{28}H_{22}$	347 nm	455 nm
bis-MSB	$C_{24}H_{22}$	345 nm	418 nm
POPOP	$C_{24}H_{16}N_2O_2$	360 nm	411 nm
PMP	$C_{18}H_{20}N_2$	295 nm	425 nm

Buck and Yeh

JUNO: LAB + 2.5 gm/l PPO + 3 mg/L bisMSB (see Boxiang Yu)

Some considerations.

- Absorption bands are ~260 nm.
- Safety considerations are driving recent choices towards high flash point.
- PC tends to be chemically aggressive.
- Compatibility with acrylic containers.
- LAB does not have a well defined H/C ratio.
- What is best for PSD performance ?
- What is the solubility ?
- Best coupling to optical windows and photo-cathodes. Best combinations.
- Size of the Stoke’s shift.

Much of this understanding and models are obtained with low concentrations. The precise behavior can shift in liquids (~10 nm) and high concentrations where strong coupling effects come into play.

Contrast with noble liquids

Noble liquids are excellent scintillators, and DUNE (Liquid Argon) and JUNO (organic-LS) will be the largest liquid scintillator detectors for a long time.

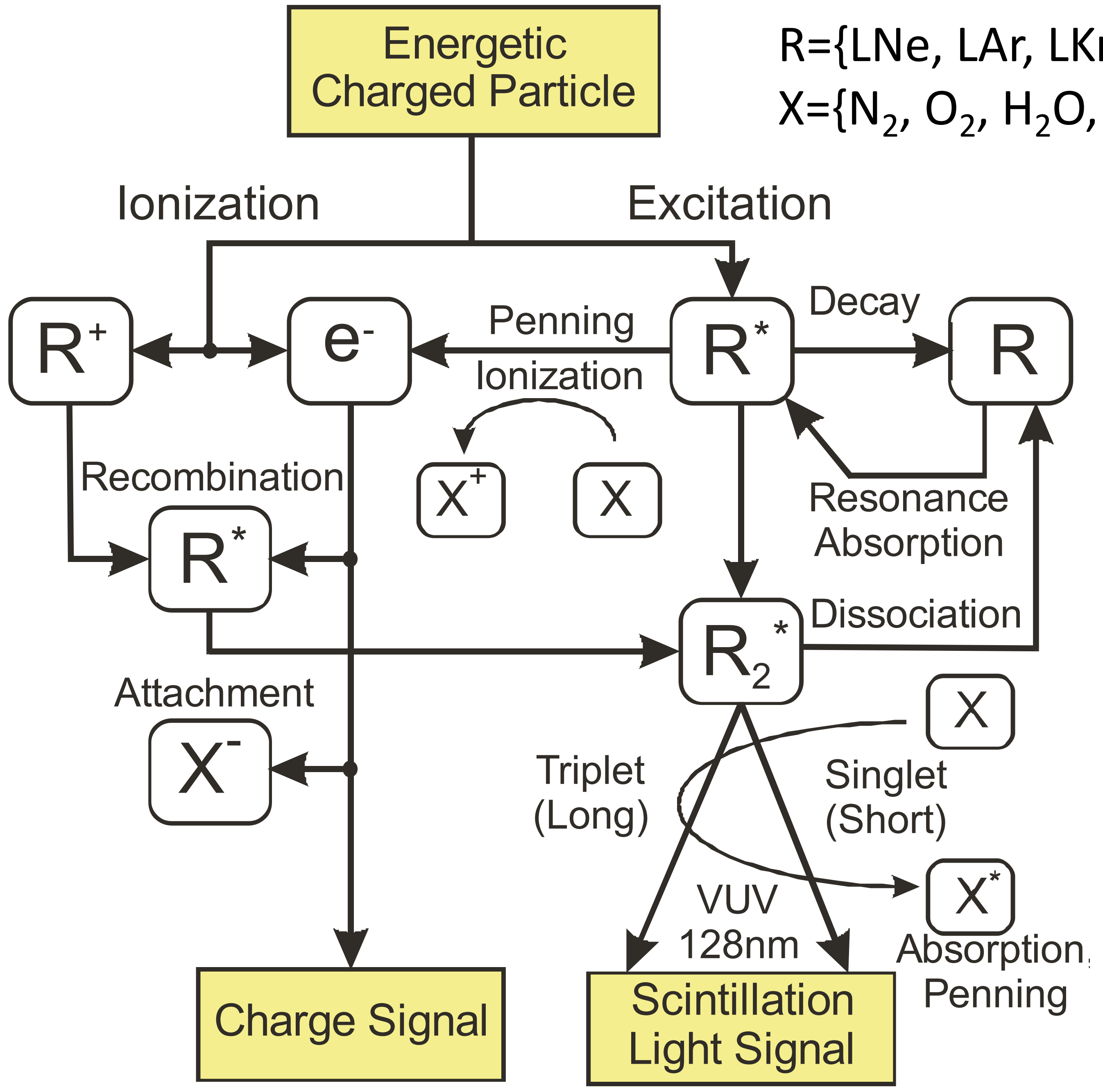
	Ne	Ar	Kr	Xe
Z	10	18	36	54
D gm/cc	1.2	1.4	2.4	3
Max Wavelength (nm)	85	128	150	178
decay time (ns) (T1, T2)	15000	6, 1500	2, 91	2.2, 27
Yield (W/O Efield) (within 20%)	30/keV	40/keV	25/keV	42/keV
boiling (K)	27	87	120	165
Radioactivity	No	Ag39 (1bq/kg)	Kr85 (high)	Remove Kr85
Cost	$$	$	$$$	$$$$

- All scintillate in the ultraviolet. Band is about ~ 10 nm wide.
- Must be shifted before a window to a photosensor
- Photosensors must operate at low temperatures.
- Yields are approximate and large.
- Triplet decay times are long for L-argon.
- TPB or PTP deposited on windows are favored shifters. But compatibility must be considered carefully for each case.

For helium singlet emission is 77 nm and may be useful to measure. Ito, Seidel (1303.3858)

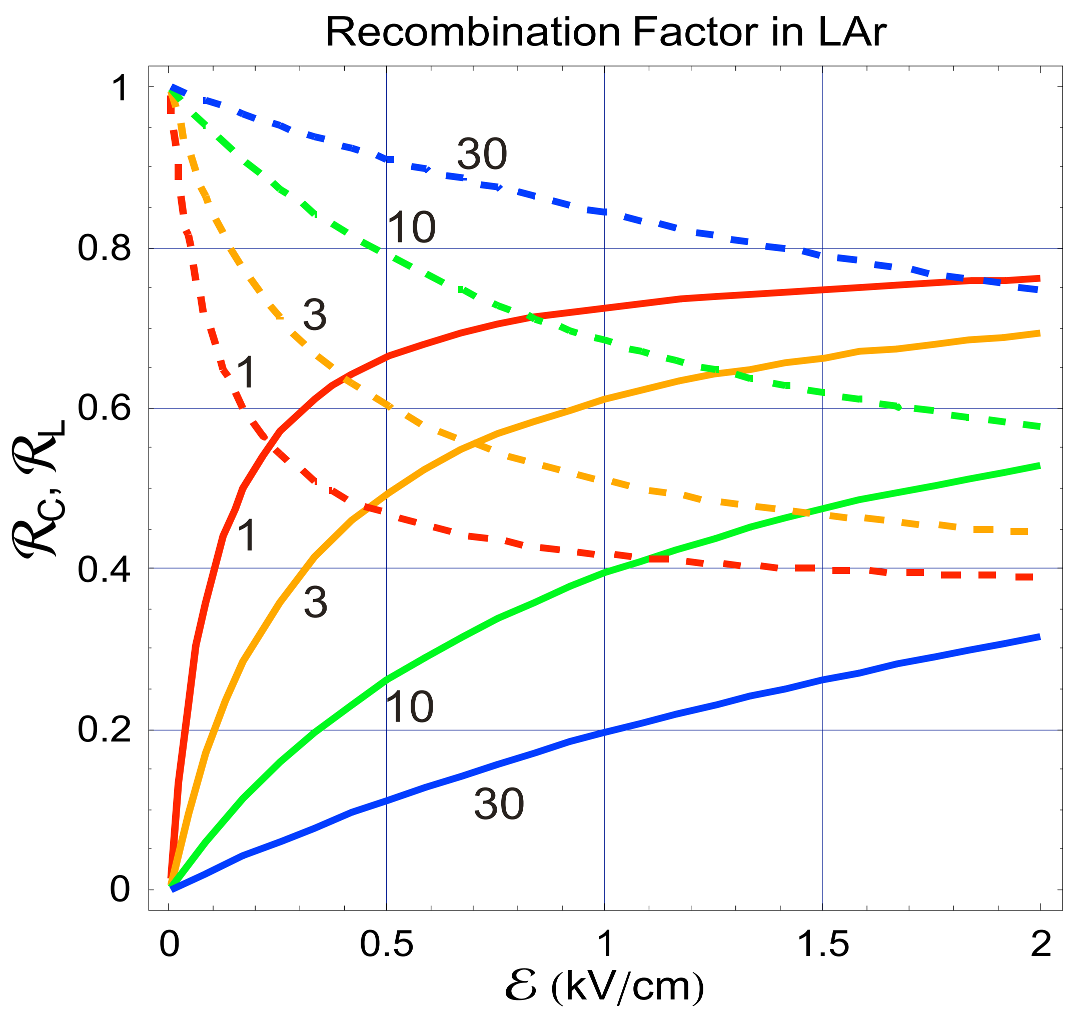
Liquid argon scintillation mechanism

Mechanism is very different from organic LS, but in practice there are commonalities



E→∞
42,000 e/MeV
8980 e/mm for MIP

E→0
51,300 ph/MeV
10,900 ph/mm for MIP
(40,000 for NaI(Tl))

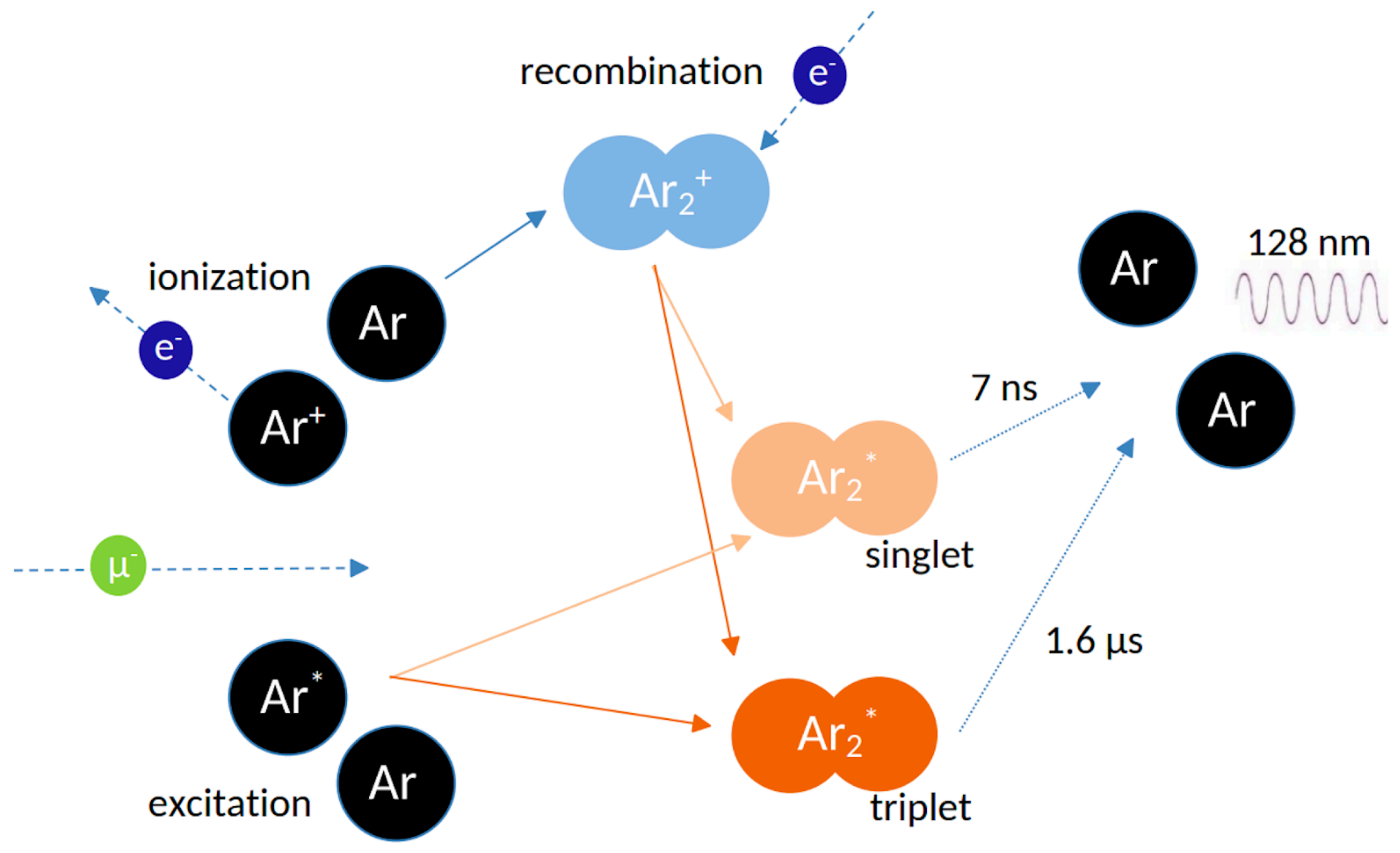


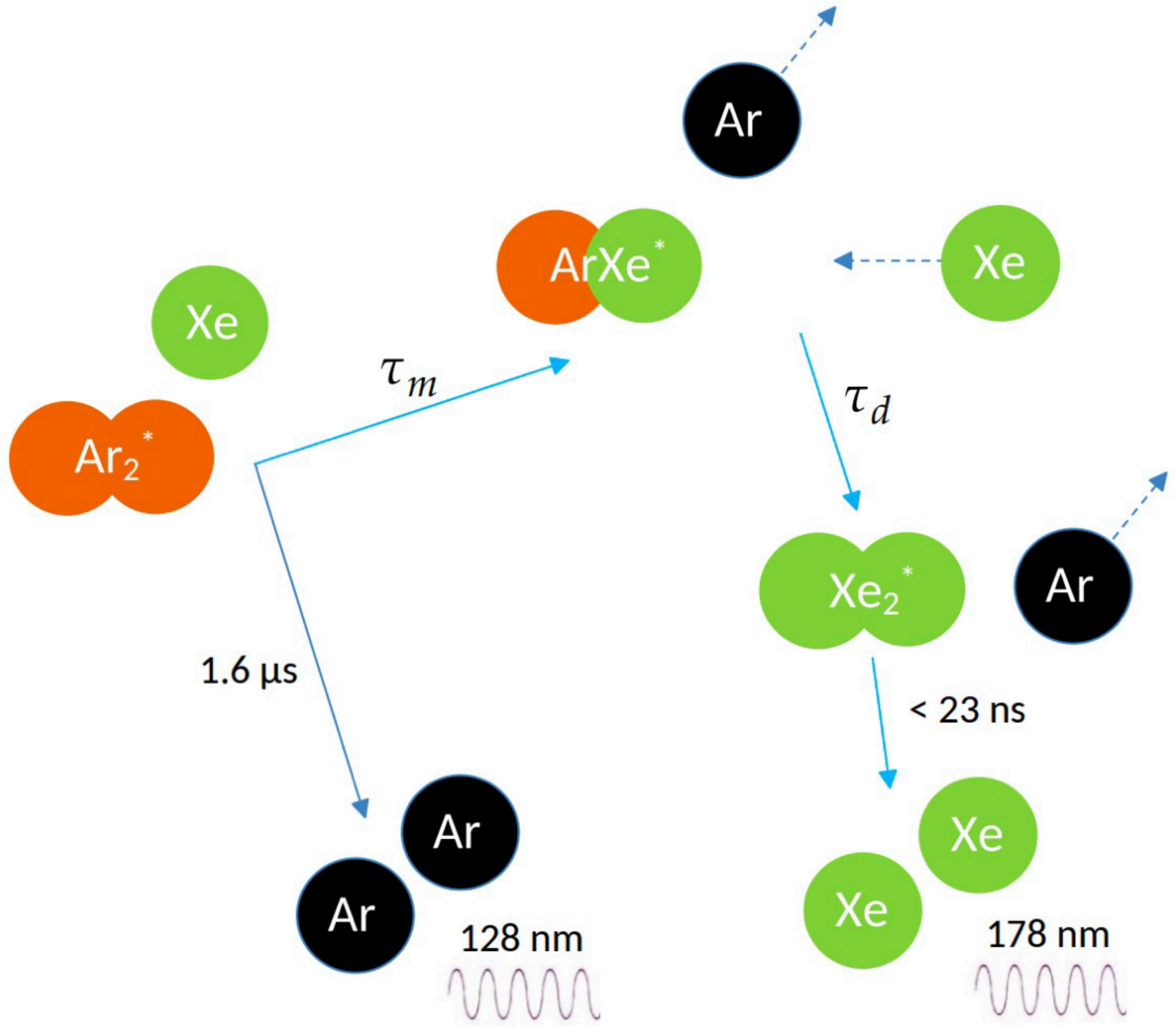
Ratio w/r/t full yield
Solid: charge, Dashed: light
Numbers: Specific Eloss in MIPs

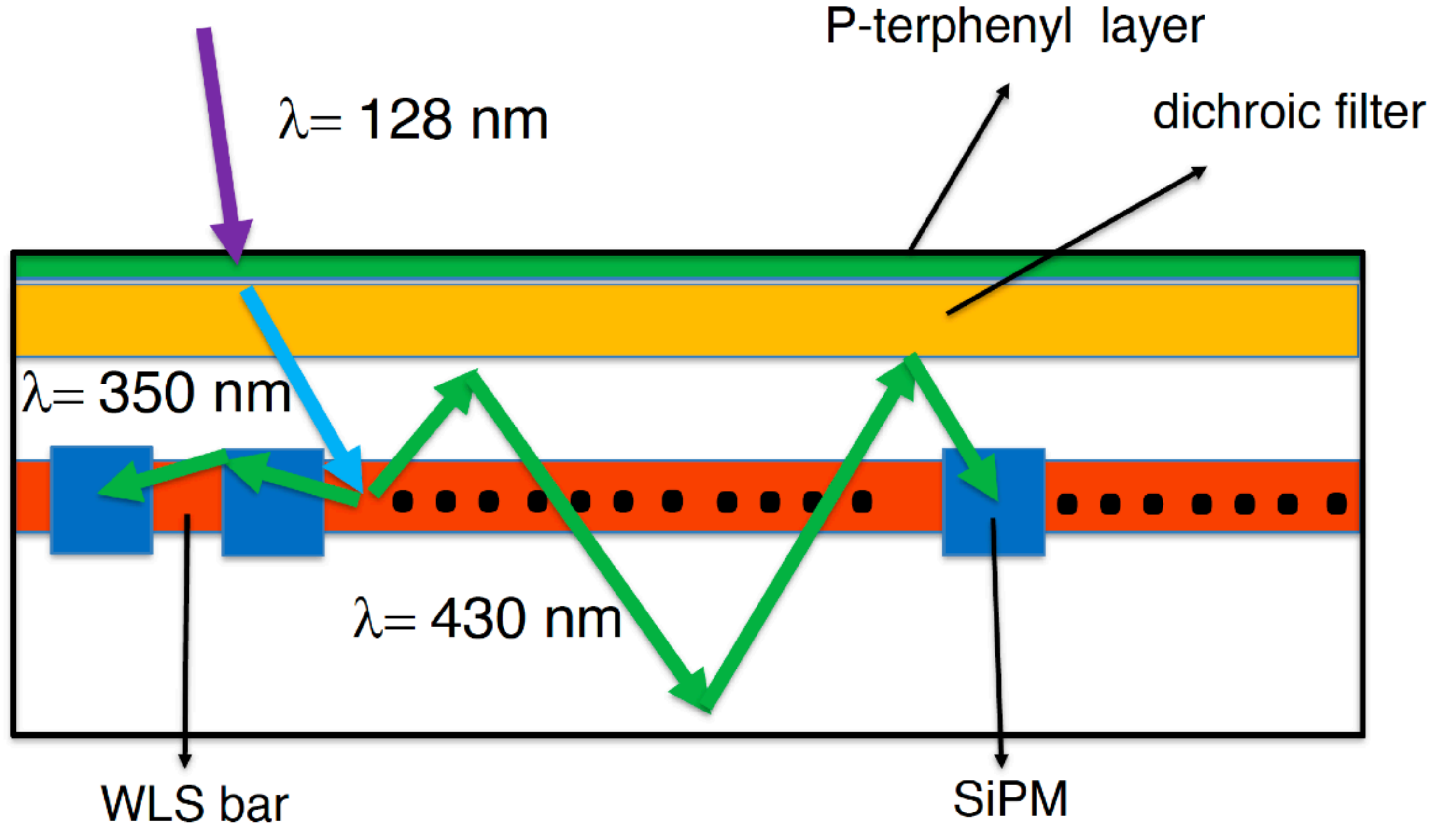
from Craig Thorn

- Argon dimer is very weakly bound, but when excited Ar_2^* or charged Ar_2^+ they are molecules with spectral features.
- Frank-Condon principle applies.
- The features are well known in gases. And known to also exist in liquids.
- Lowest states are singlet and triplet states
- The excited dimers (excimers) are only created by ionization and so the liquid is transparent to its own scintillation light (even it deep UV).
- The energy can also be coupled to Xenon dimers in a unique manner. This has been proven on a large scale in the DUNE prototypes.

Shifting liquid argon light







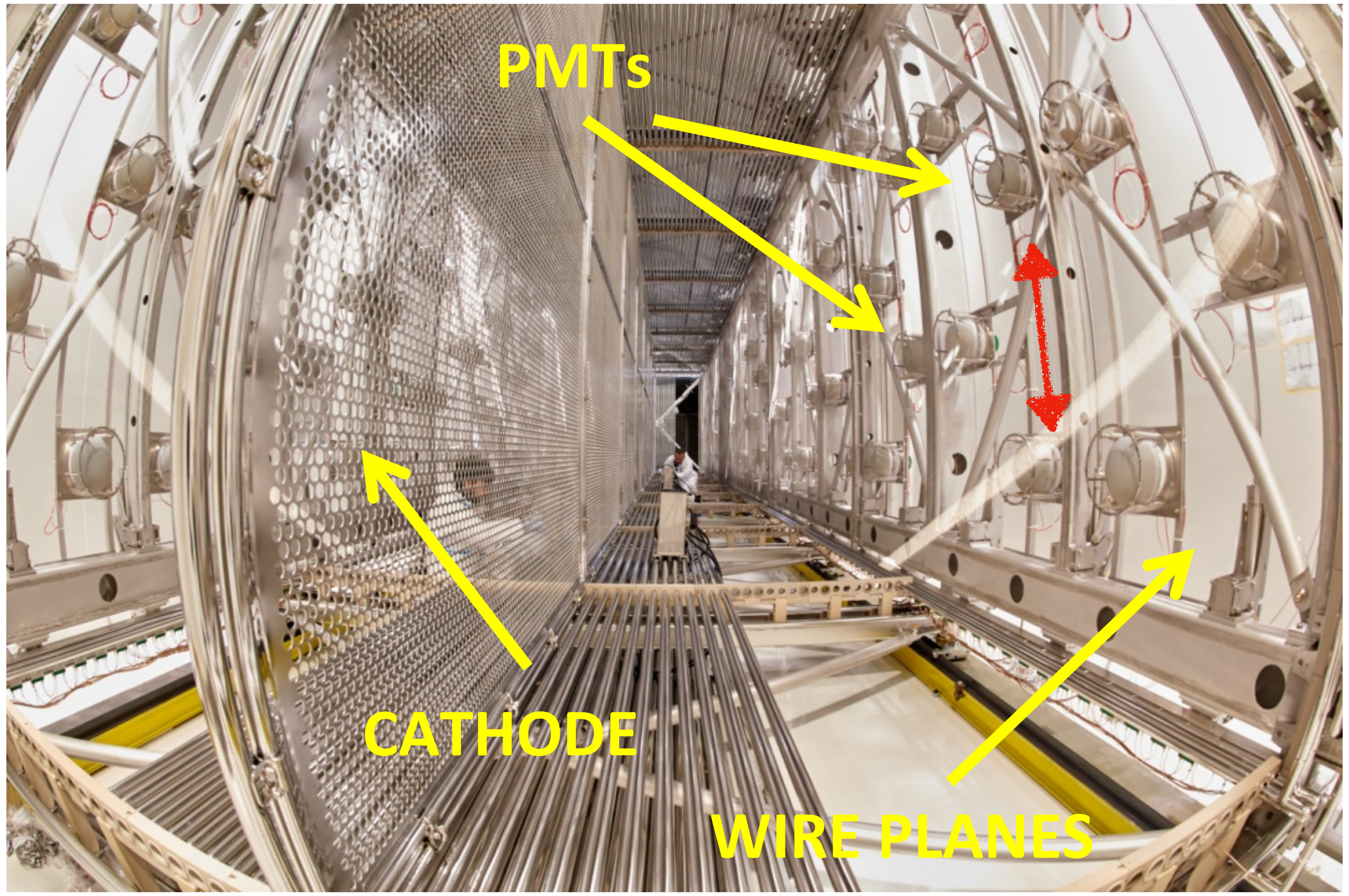
x-ARAPUCA concept
see Segreto and Machado

Xenon doping

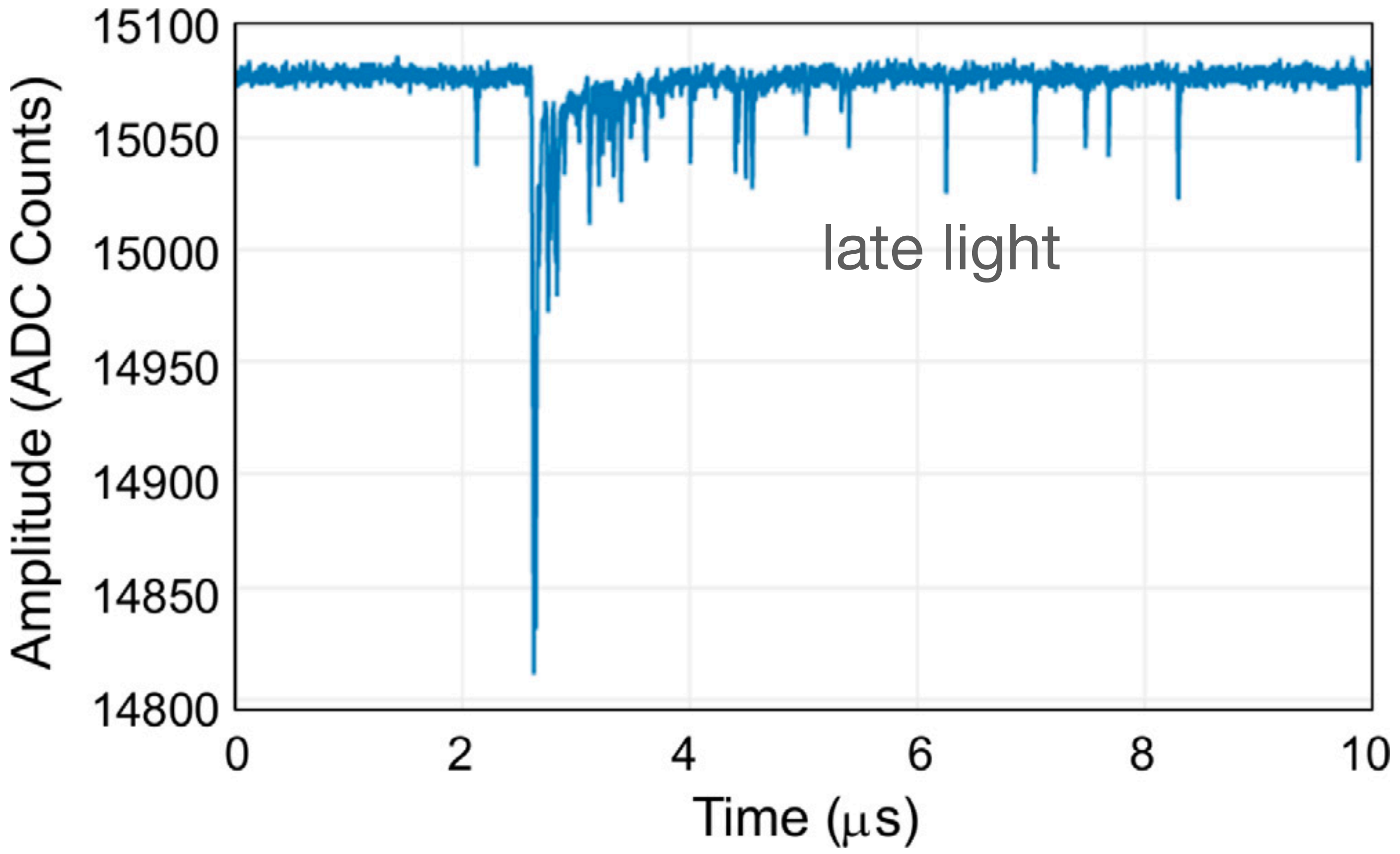
- ~ few hundred ppm
- Moves the scintillation wavelength to 178 nm
- Reduces the effective triplet (long) timescale to ~50-100 ns

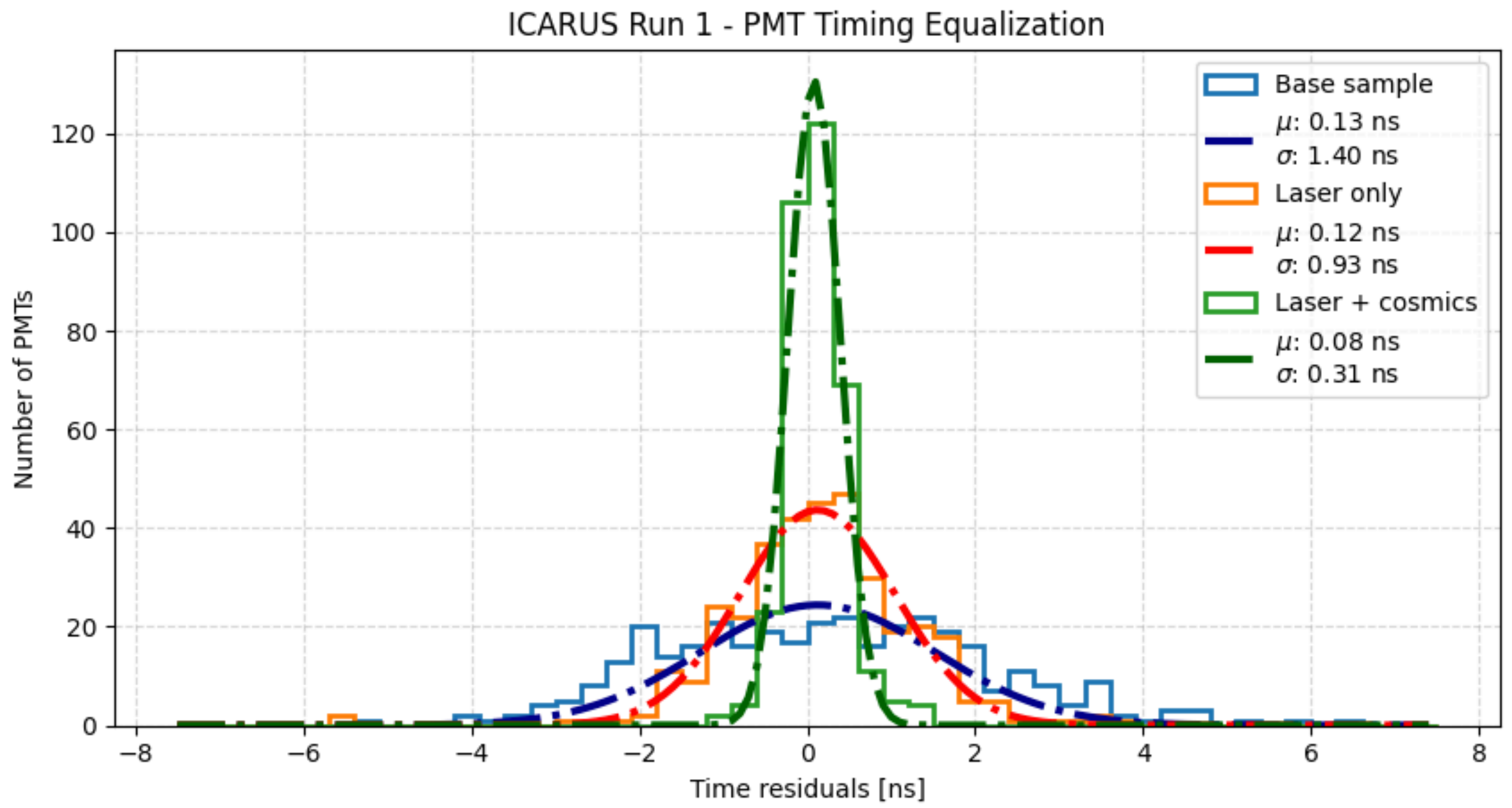
Noble liquid scintillation detector practice. (ICARUS)

- ICARUS T600 at Fermilab is currently the largest liquid argon scintillation counter.
- 90 PMTs are mounted behind anode wires. Total 4*90 = 360 channels read out with 500 Mhz ADCs. Efield = 500 V/cm
- Uses 8 inch R5912-mod PMTs with TPB coating.
- Coverage is ~ 5%. Yield ~50 pe/MeV.
- After laser and muon calibration relative time calibration is ~ 300 ps
- PMTs will be used for tracking and muon rejection and beam timing.



~1 meter

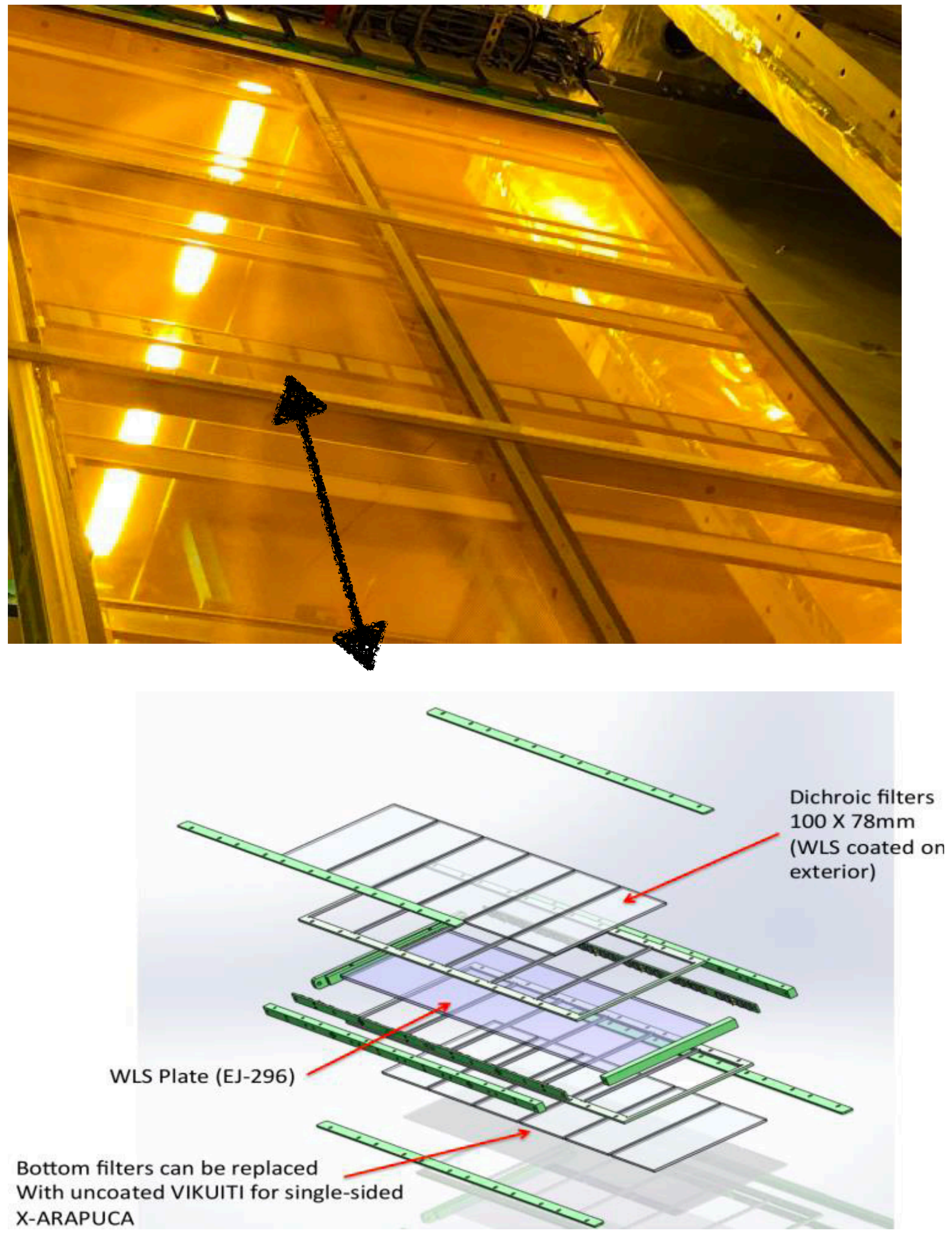


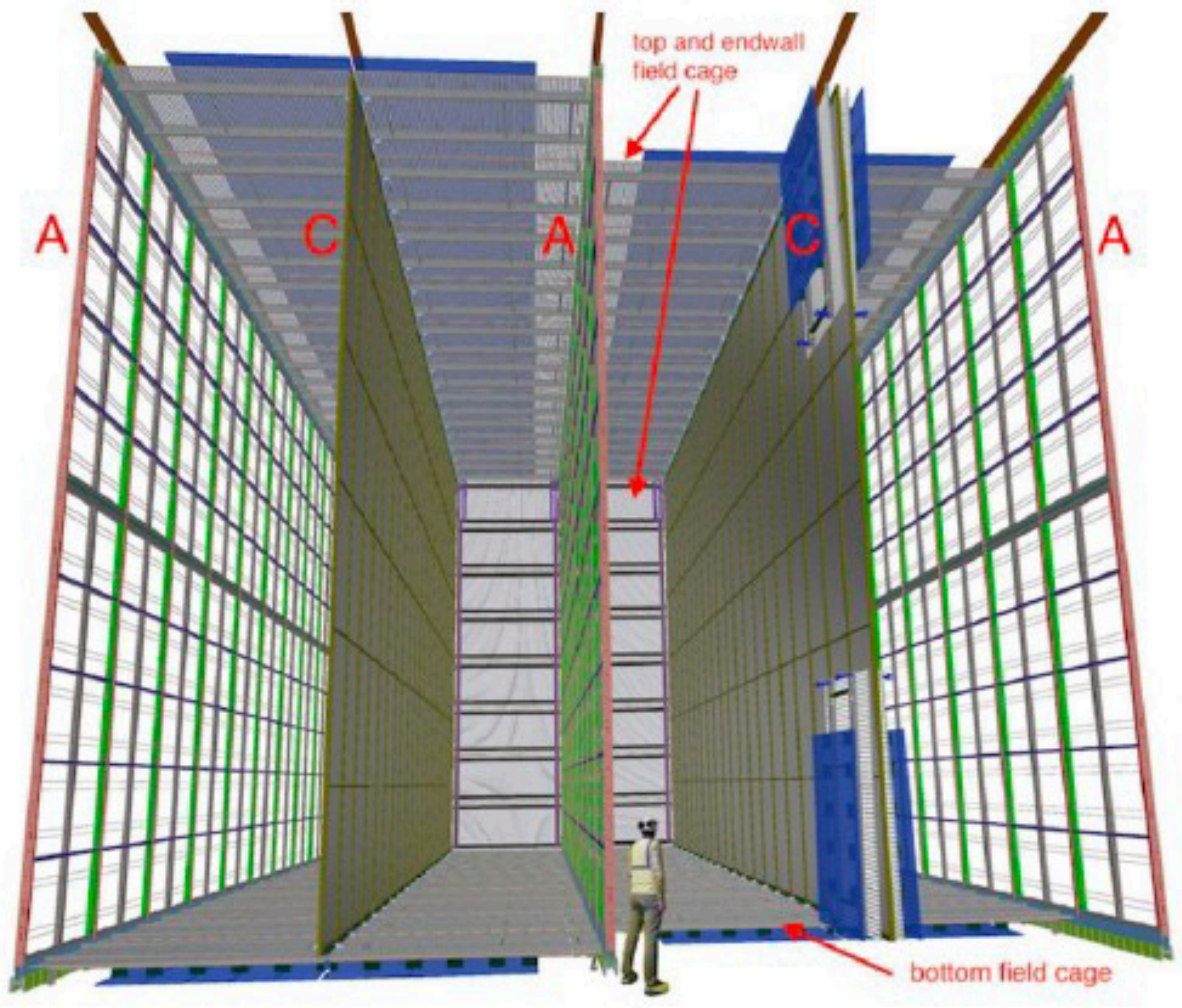


See talk from Patrick Green on microBoone performance on accelerator beam timing

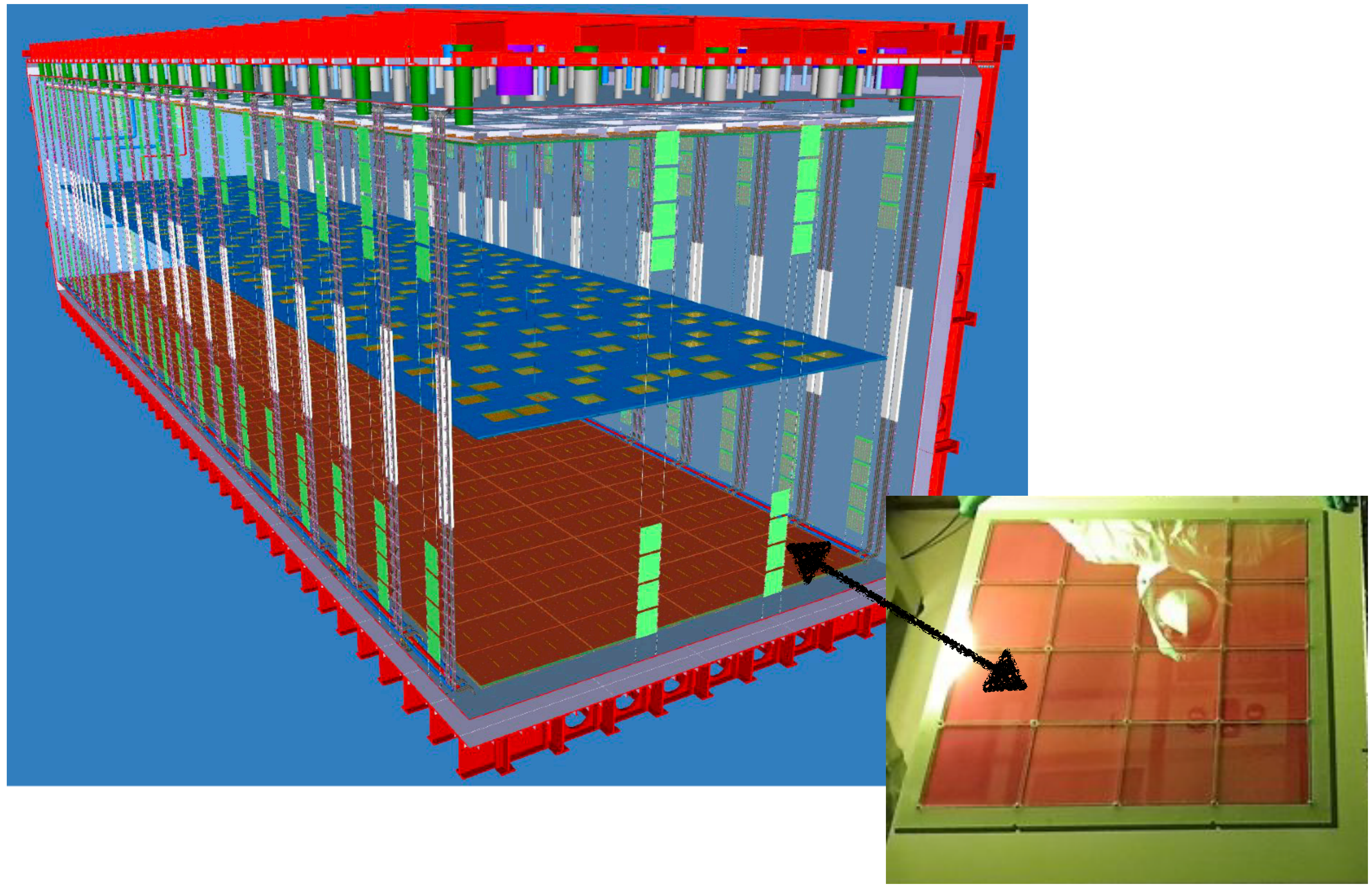
DUNE experience with x-ARAPUCA

The photon trapping system using dichroic filters will be the detection system for DUNE.





Horizontal drift detector



Vertical drift detector

- Photon detection efficiency for each detector is estimated to be ~ 2% (for photons that are incident)
- For Vertical Drift detector, the total collection is estimated to be ~ 30 p.e/MeV (without xenon doping)
- See talk by Francesco di Capua

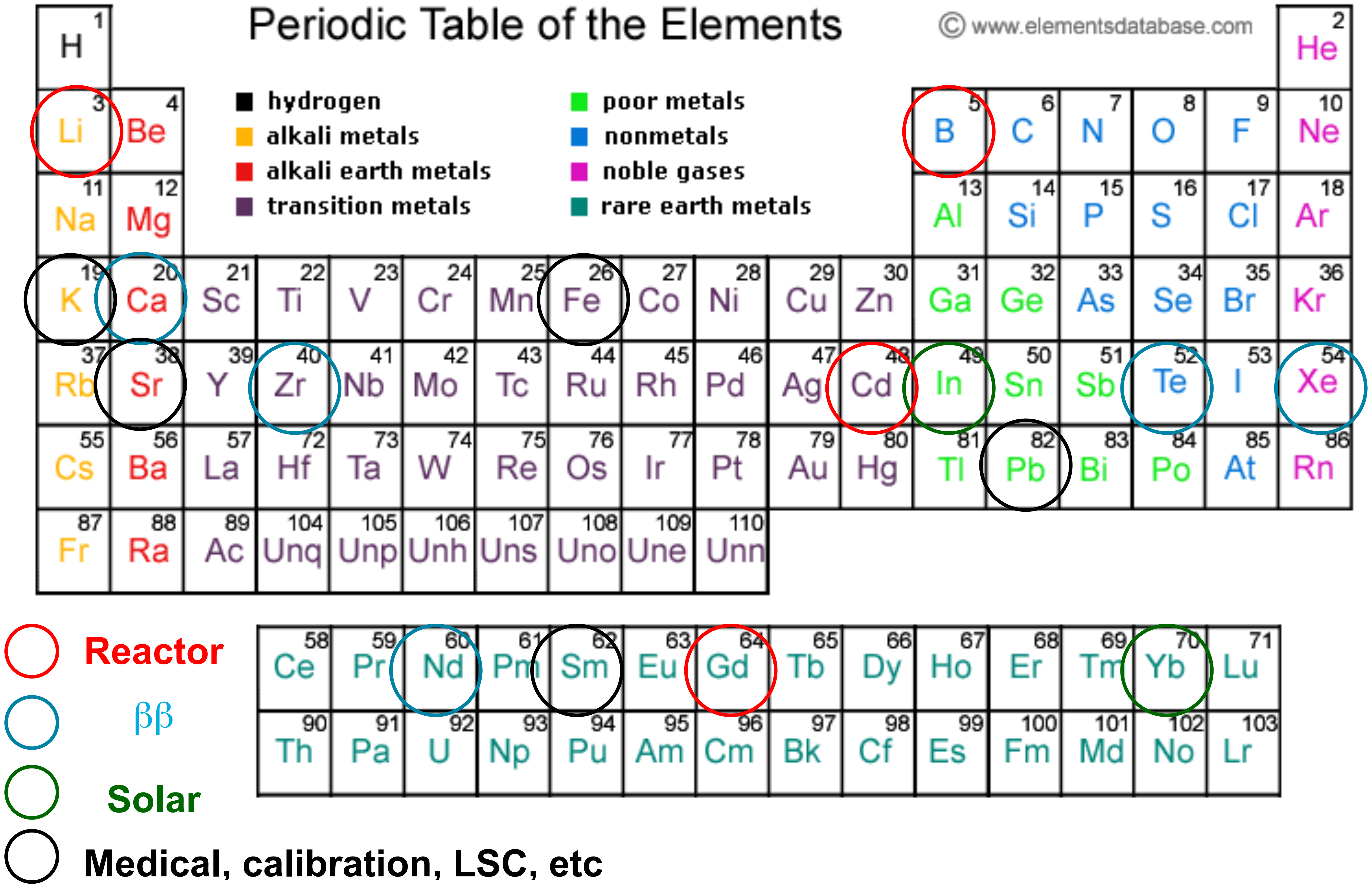
Metal-doped Organic Liquid Scintillators for neutrino physics and other frontiers.

Cd loading used by Reines and Cowan for the detection of reactor neutrinos.

Many years of advancement in Nuclear separation chemistry.

Two mature methods: Carboxylates and beta-diketonate. Each case must be examined for:

- *high transparency*
- *high light yield since energy can be lost non-radiatively at high loading.*
- *high radio-purity*
- *Long term stability.*



A water based scintillator can expand number of candidates that can be loaded effectively.

Brookhaven National Laboratory

The practice of metal loading.

Table 5. Selection of metal loaded scintillators used in reactor neutrino experiments. The attenuation length is given in the region 430–440 nm and the light yield in % of anthracene.

Experiment	Solvent	Metal	System	Ligand	att. (m)	Light yield	
Sav. River	TEB/oil	Cd	carbox.	2-ethylhex.(C_8)	2 m		
Bugey	PC	^6Li	carbox.	salicylate	2.6 m	31	0.15 wt%
CHOOZ	IBP/paraffin/ hexanol	Gd	nitrate	$(NO_3)_3$	4 m	35	0.9 wt%
Palo Verde	PC/oil	Gd	carbox.	2-ethylhex.(C_8)	10 m	56	0.1 wt%
Double Chooz	PXE/dodec.	Gd	β-diketone	THD	10 m	38	0.123wt%
Daya Bay	LAB	Gd	carbox.	TMHA (C_9)	15 m	50	0.1wt%
RENO	LAB	Gd	carbox.	TMHA (C_9)	10 m	48	0.1 wt%
Prospect	DIN	6Li	WbLS		~0.85m	80	0.08wt%

Buck, Yeh (2016)

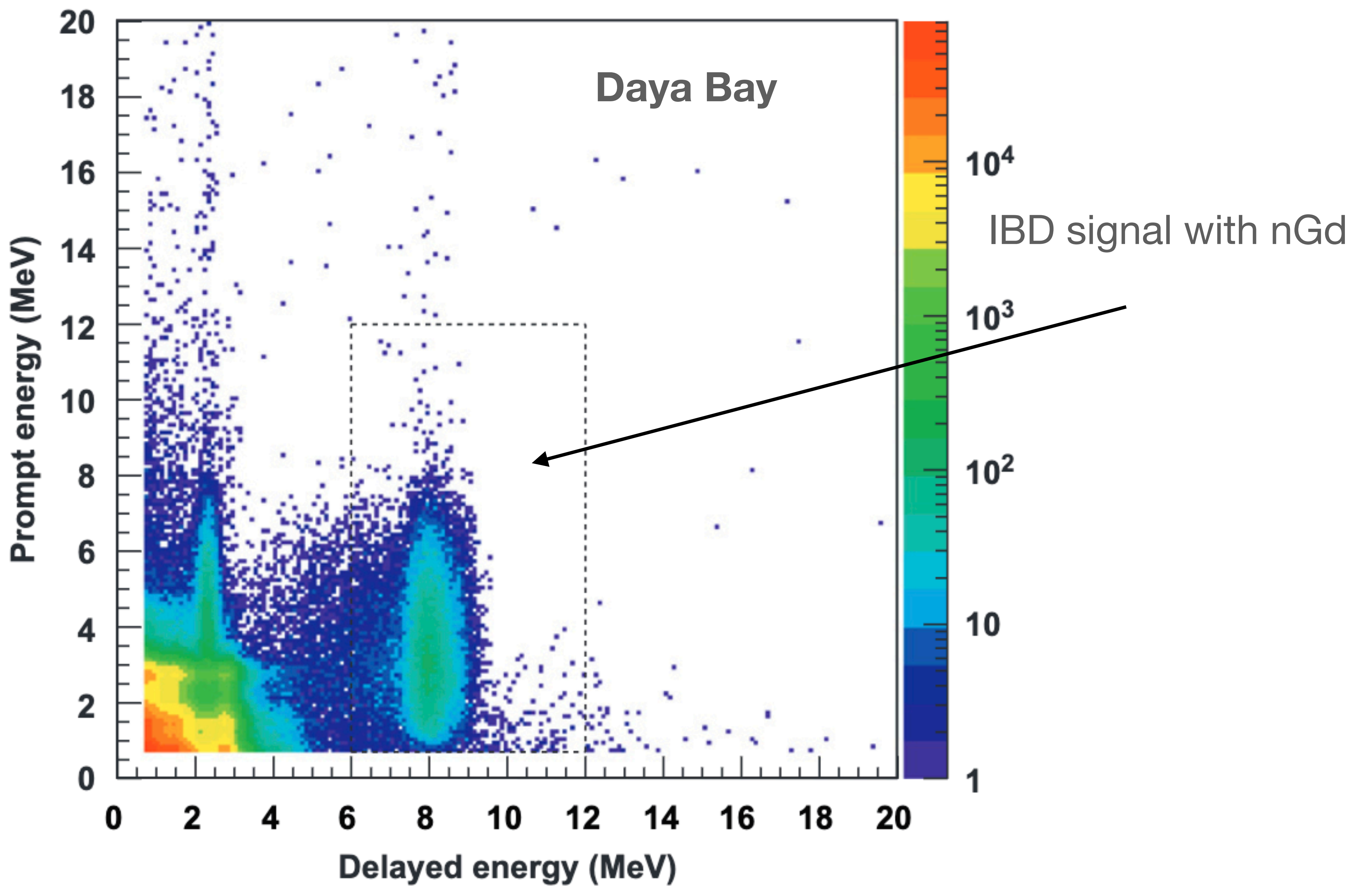
Each of the early experiment contributed to the development of the metal loading technology.

Early issues: compatibility with containers, stability in transport, loss of attenuation length due to contamination and oxygen exposure.

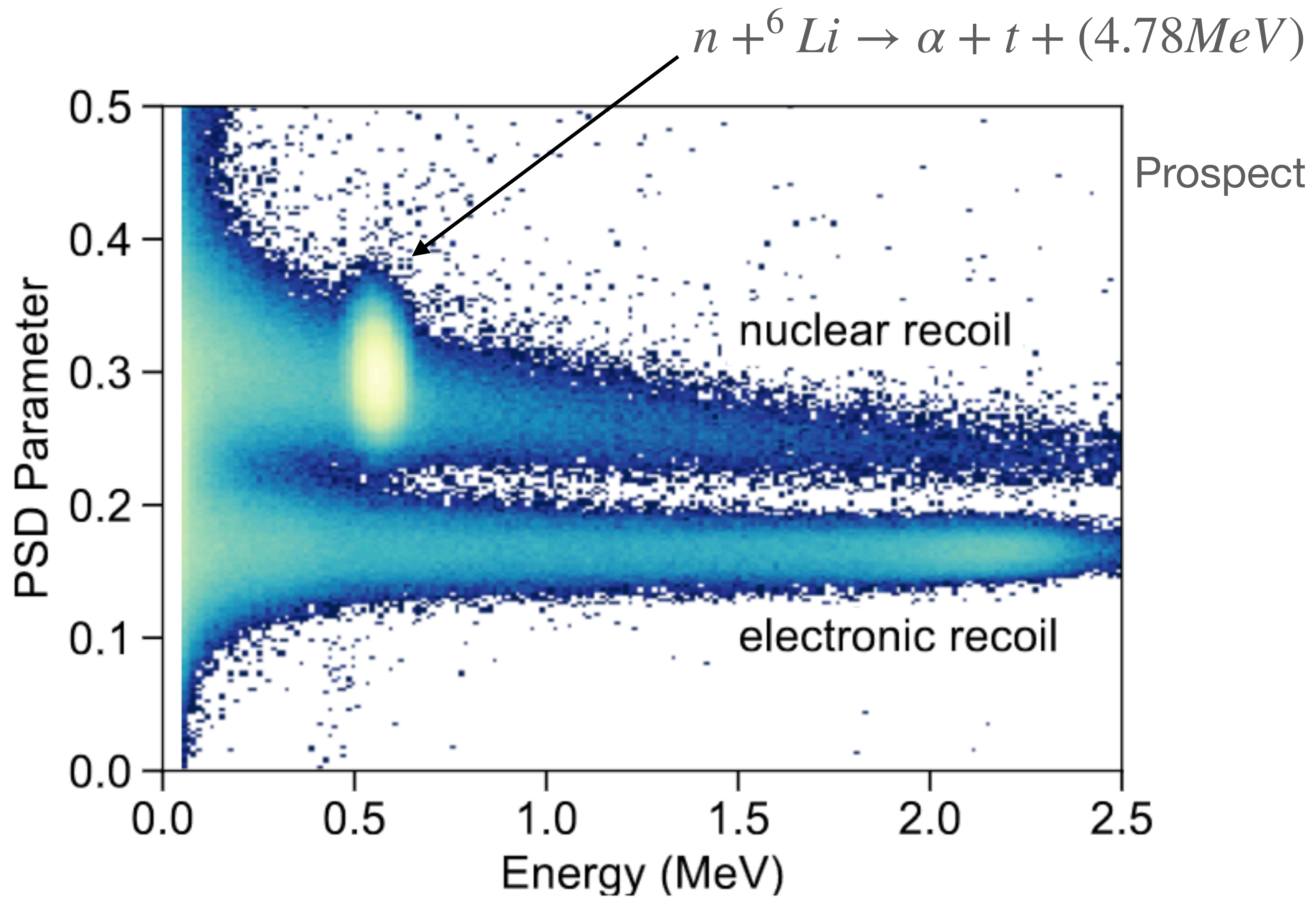
The maturity was obtained with DC, DB, and Reno, and the discovery of that the electron neutrino is a 3-neutrino state.

The PROSPECT experiment obtained high light yield and excellent PSD with the WbLS method of loading Lithium 6. GDLS has also been used for dark matter, LZ, for veto.

Recent example performance



Daya Bay: NIM A685 (2012) 78-97 (~150 meters of overburden)



PROSPECT: 1805.09245
minimal (few mwe) overburden

$$PSD = \frac{Q_{tail}}{Q_{full}}$$

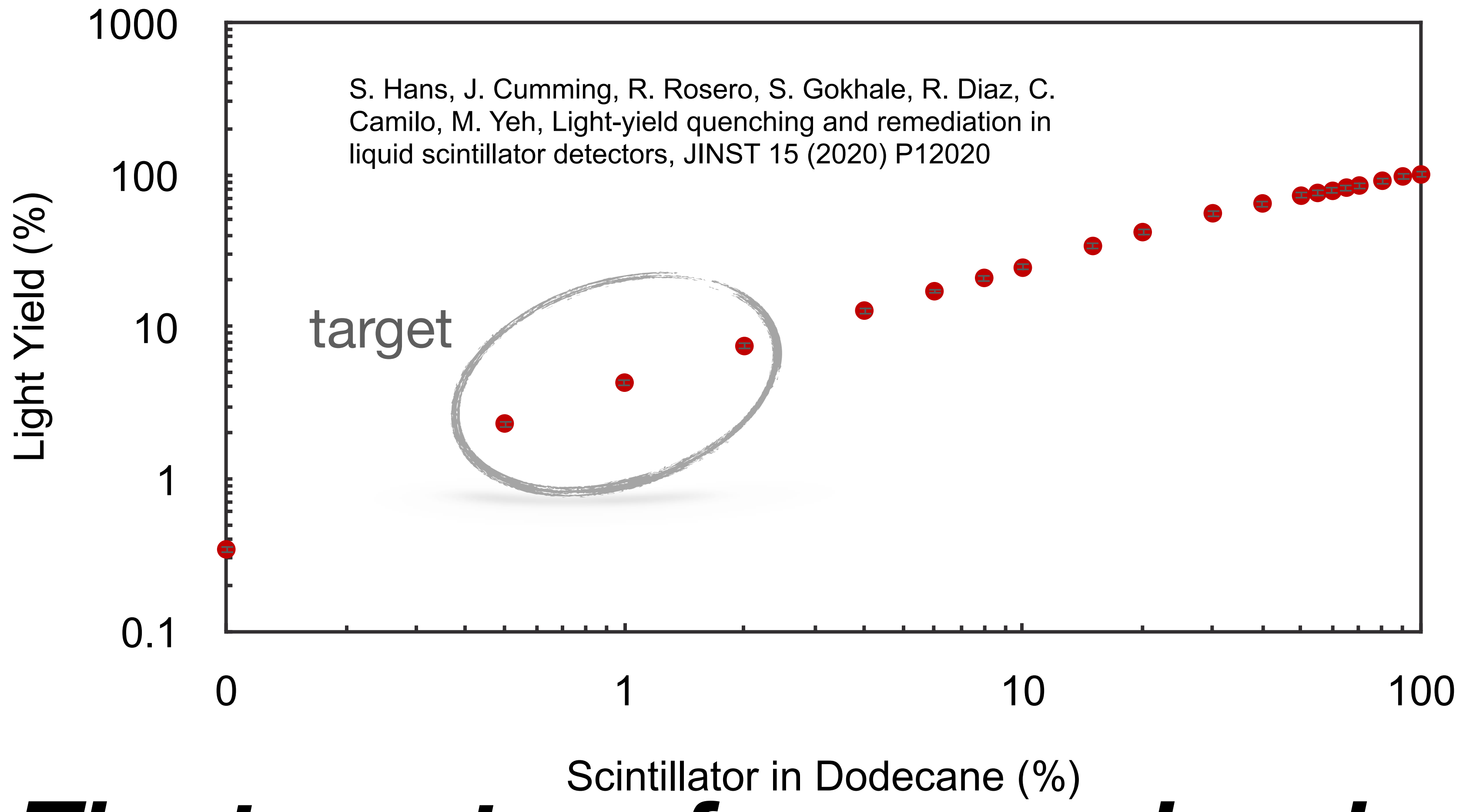
Qtail: 40-120 ns

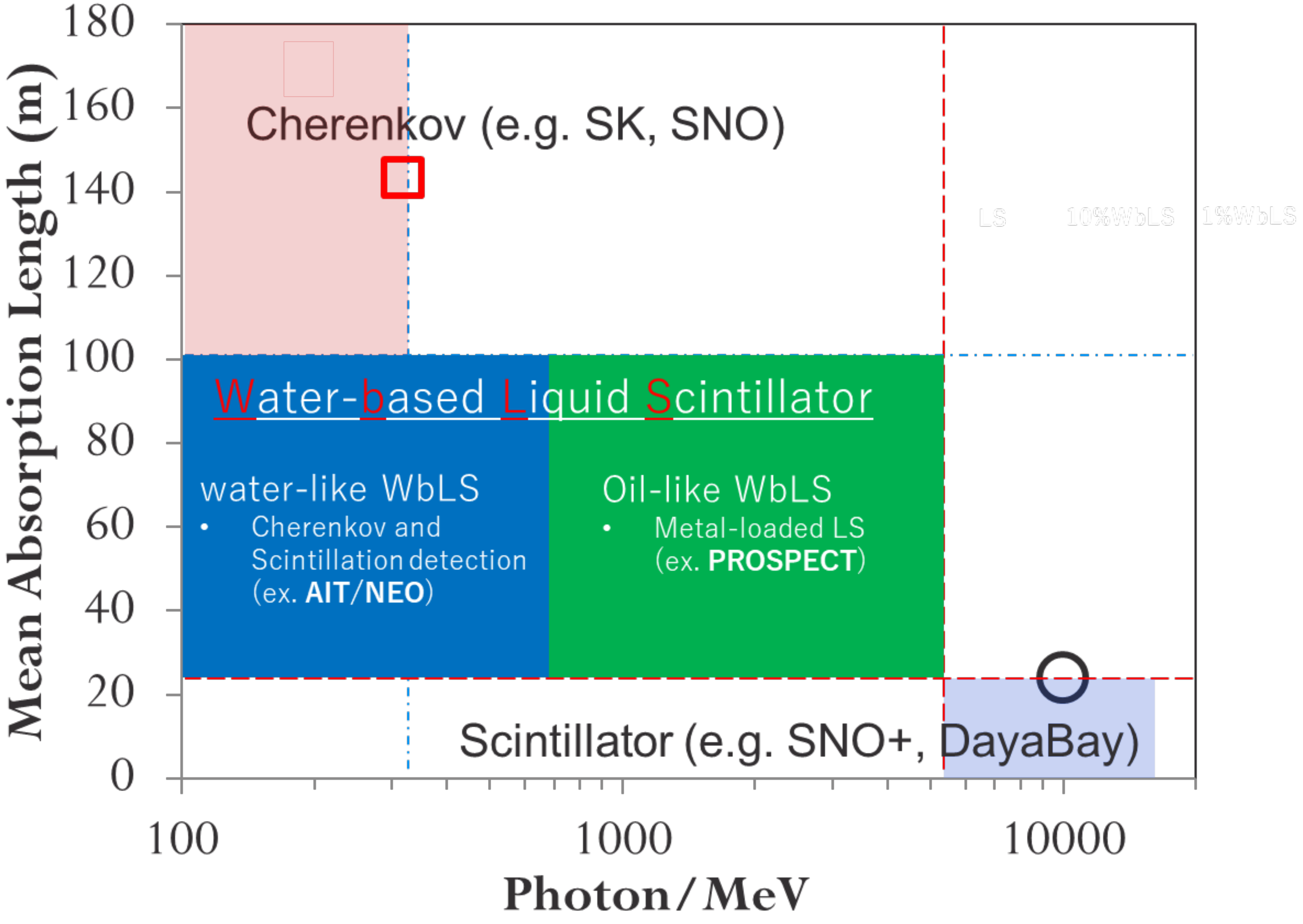
- ***Recent performance in Daya Bay (left) , and PROSPECT experiments (right)***
- ***LY: PROSPECT: ~8200 photons/MeV (850 pe/meV), ~ 5000 photons/MeV (~170 pe/MeV)***
- ***Many recent experiments with Gd-loaded-LS have been successful: NEOS (South Korea), NEUTRINO4(Russia), STEREO (FRANCE).***
- ***Metal loading has enabled near surface reactor neutrino detection with minimal shielding***

Water-based liquid scintillator development

Focus on development in the US.

- A novel low-energy threshold detection medium, bridging scintillator and water.
- Tunable scintillation light from ~pure water to ~organic.
- Environment-friendly, noncombustible, and excellent material compatibility; feasible for **field study**.
- A particle detector capable of Cherenkov and Scintillation detections
- Viable for metallic isotopes loading for enhanced detections (**neutron-enhanced**)





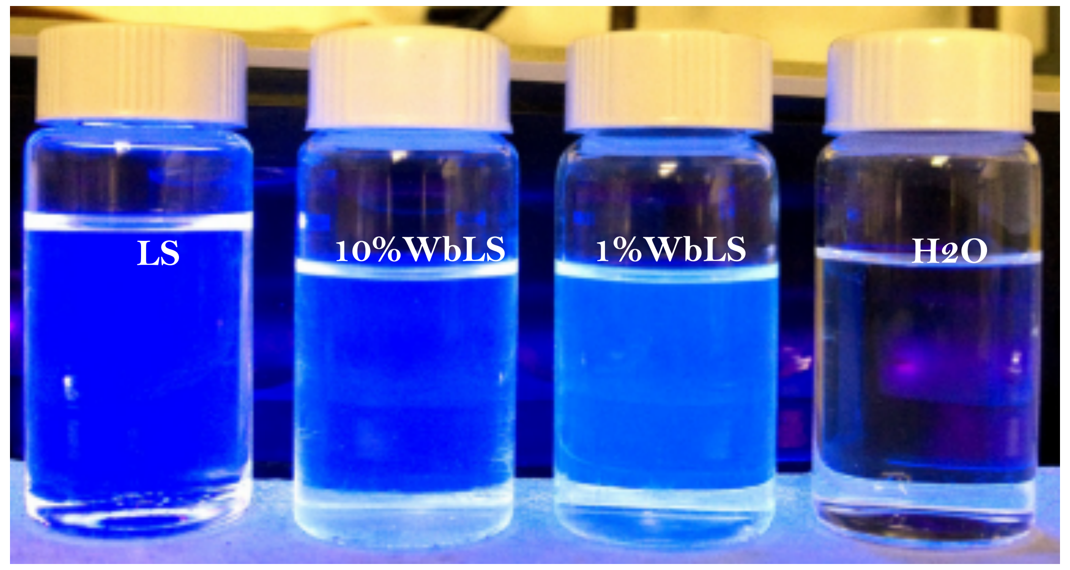
proposed for proton decay and neutrino detection: NIM A660 (2011) 51-56

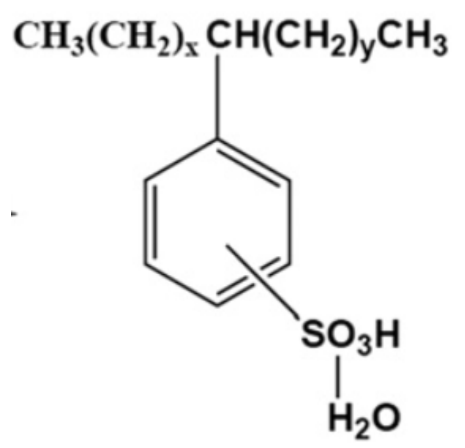
- ***The target performance has been achieved, stability and scaling is being examined.***
- ***Many groups are collaboratively engaged in this R&D.***

WbLS status and progress.

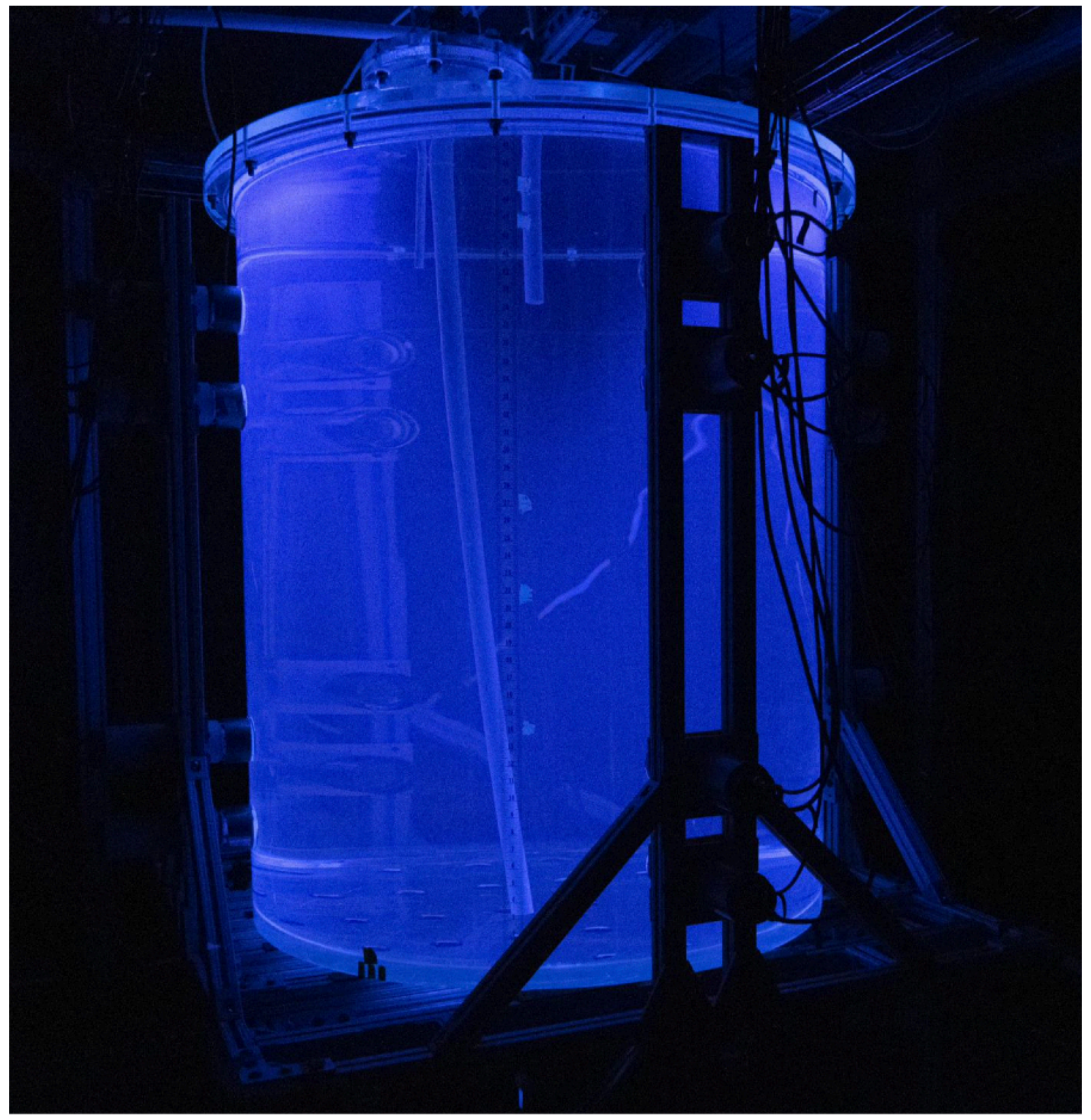
Current status in US. There is a world-wide effort towards similar technologies.

- Technique based on lipophilic & hydrophilic surface active agents (LAS). R&D started in 2010. The energy has to
- Samples have been stable for many years.
- A 1 ton R&D prototype has been operating for 1 year with excellent results.
- Scale-up demonstration projects are being constructed at LBL (4 ton EOS) focused on event reconstruction) and BNL (30 ton) focused on recirculation and purification.
- EOS and 30 ton data will be available by end of 2025
- Excellent candidate technology for low cost nuclear reactor monitoring. Funded through non-proliferation initiatives.
- Also considering heavy water based liquid scintillator

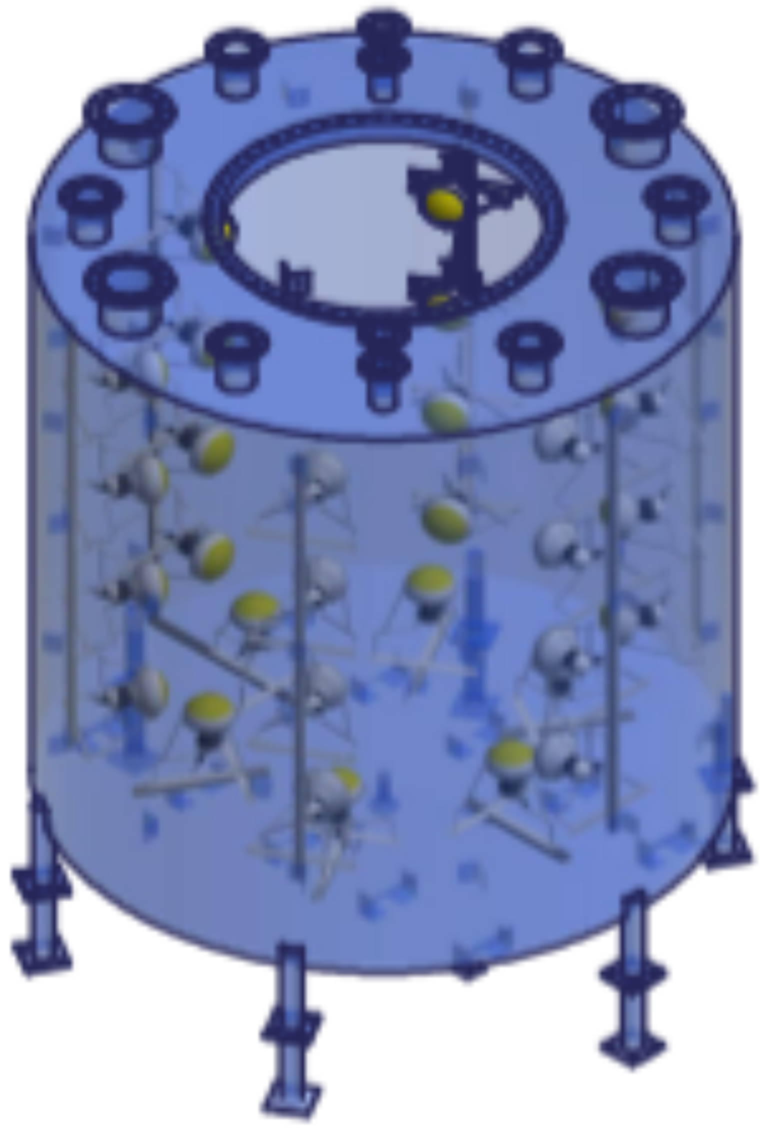




LAB based + PPO



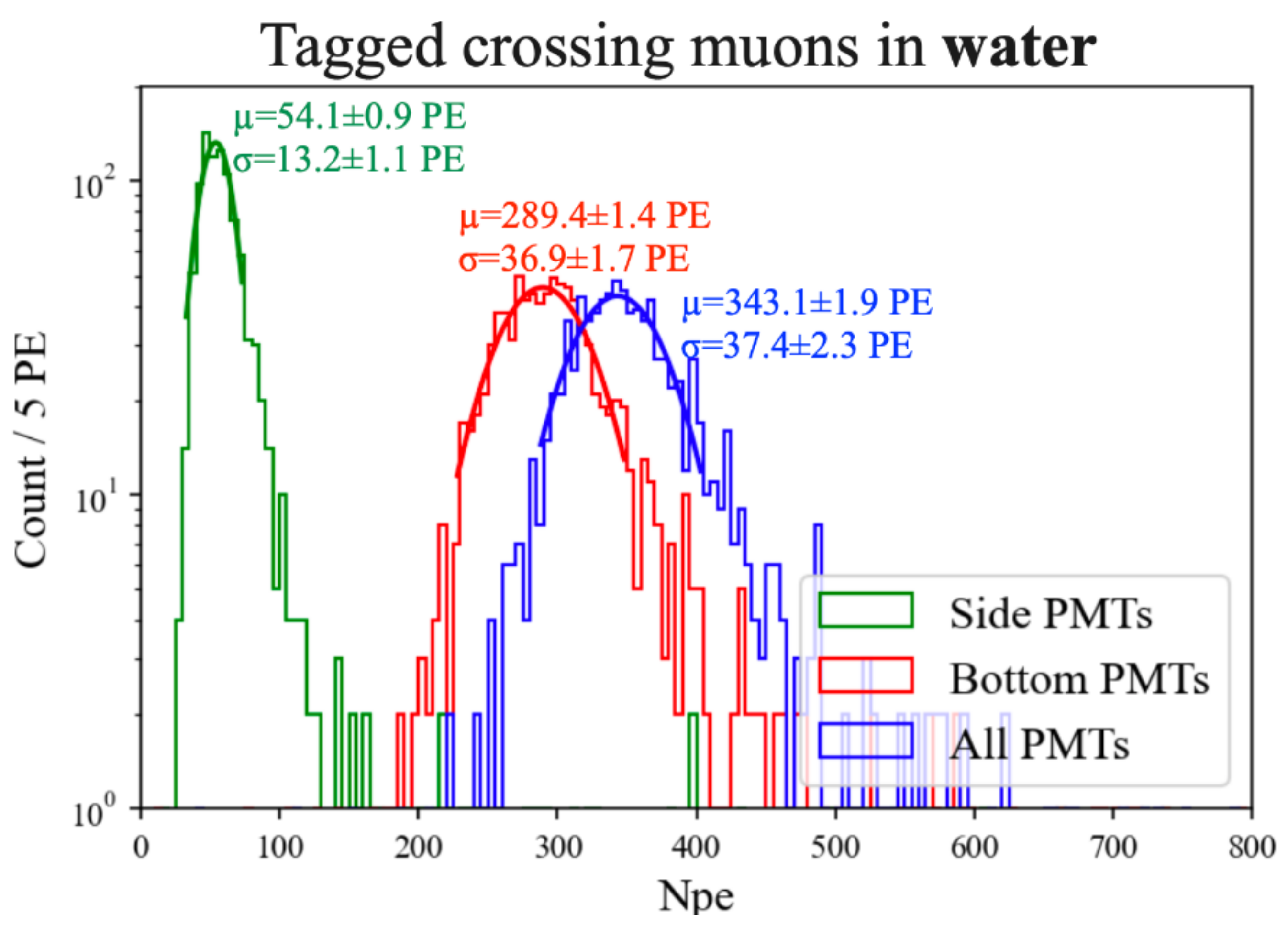
30, 2 inch bottom, and 28, 3 inch side PMTs



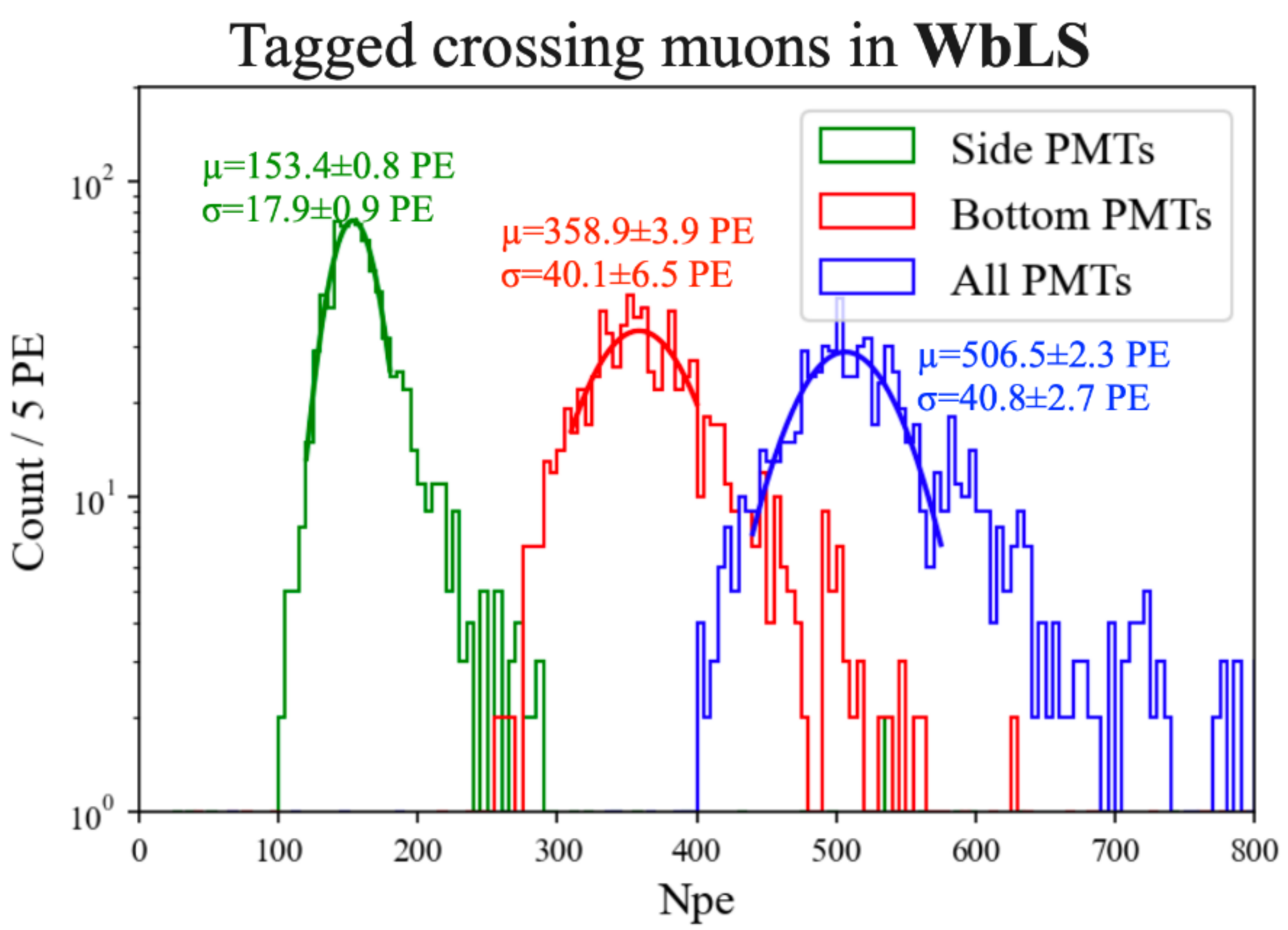
30 ton design will have all elements of a kiloton class detector.

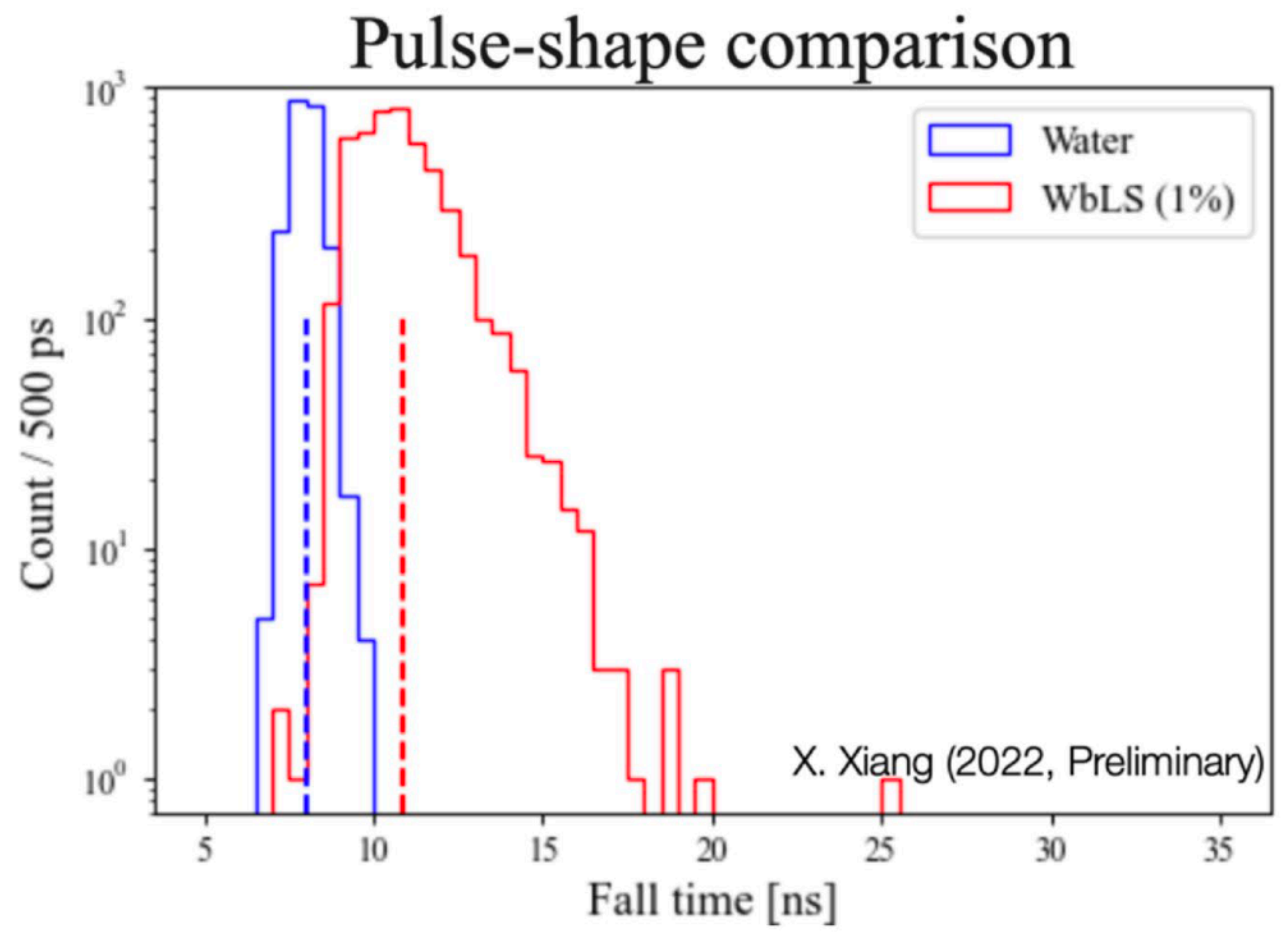
Data from scaled up investigation of WbLS (1ton)

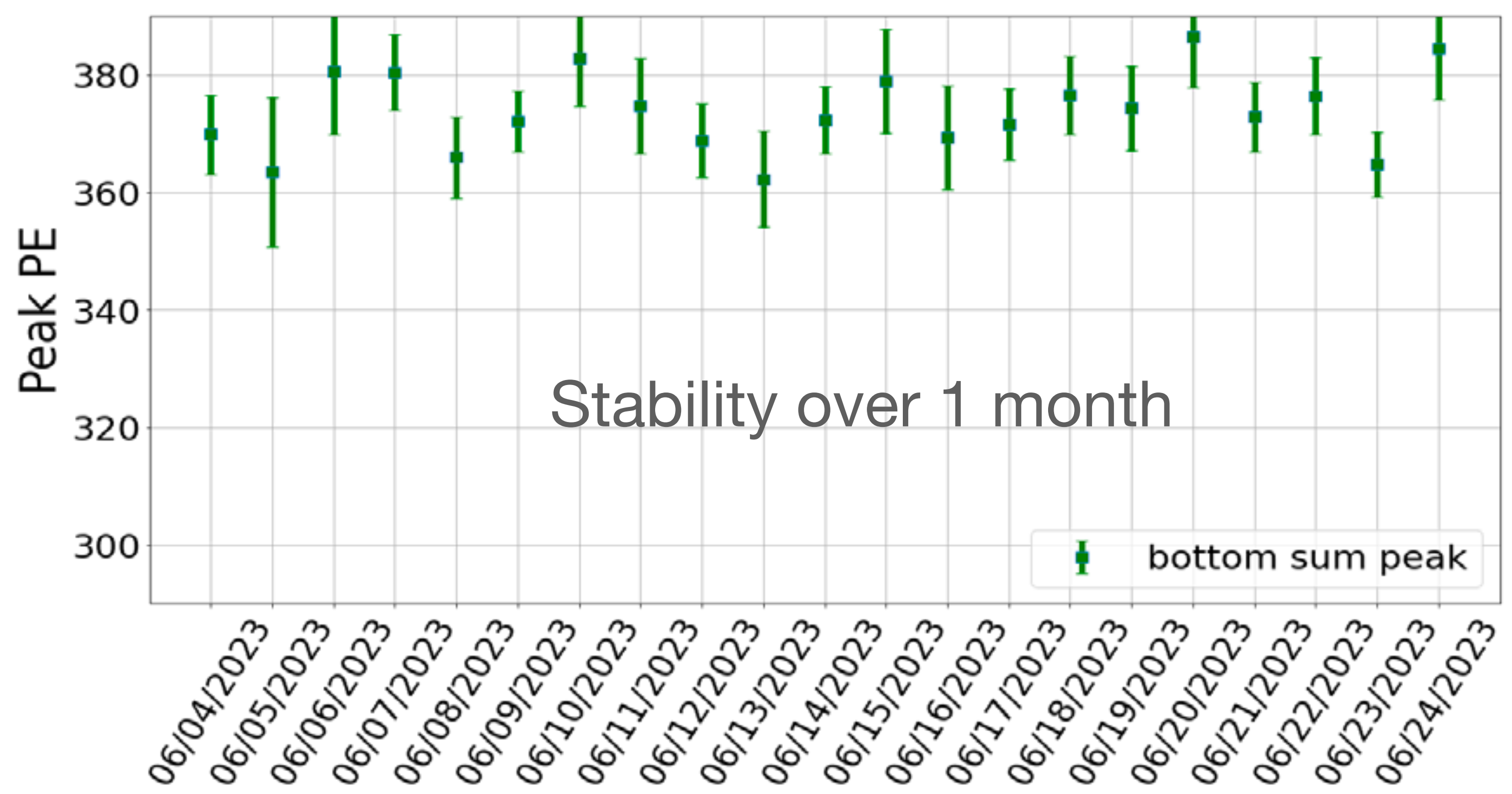
Well defined through-going muons provide a peak on the bottom and side PMTs



Inject 1%
LAB-PPO







Stable signal for Cherenkov versus scintillation has been achieved.

Clear separation in pulse shape.

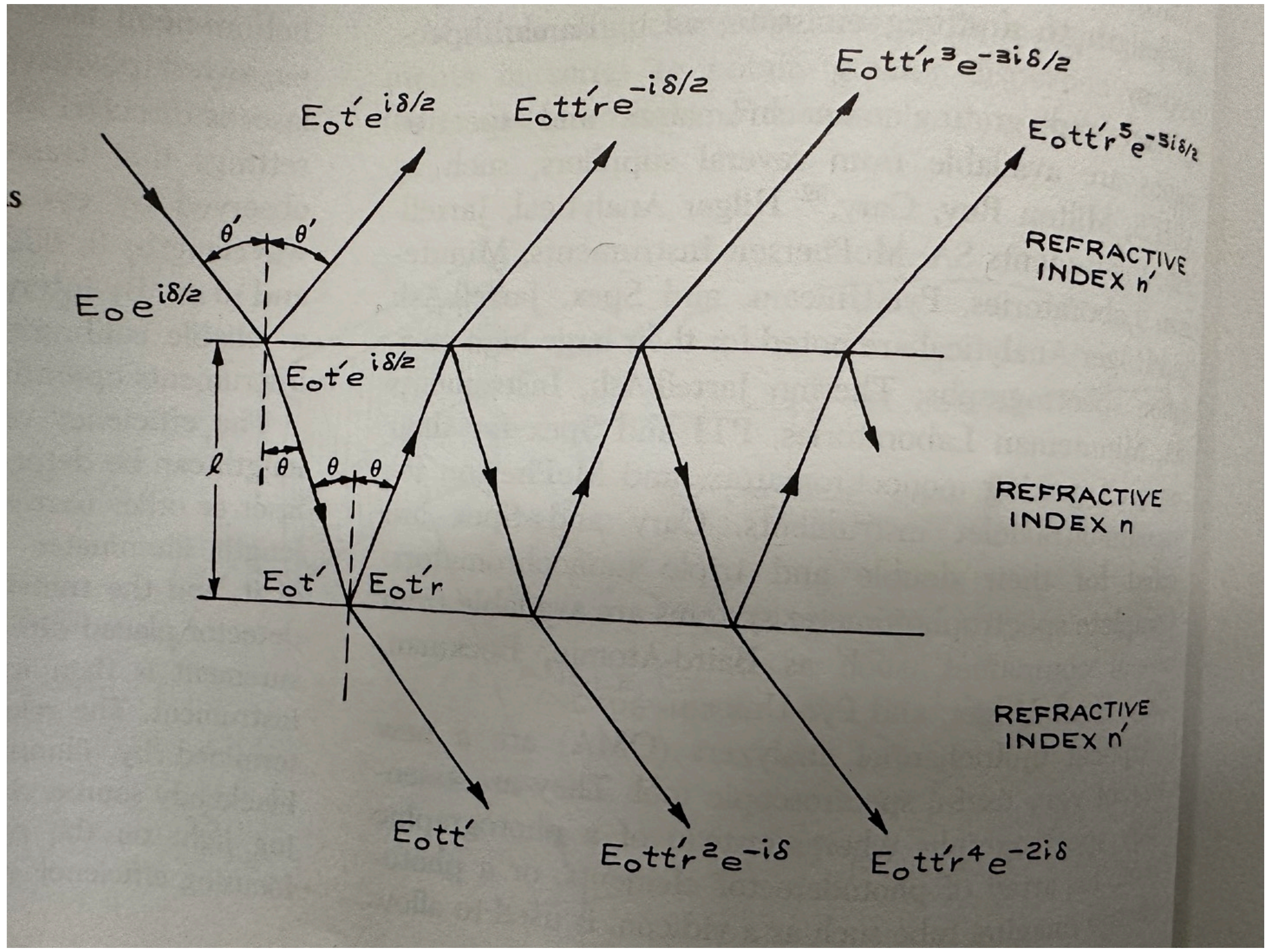
Analysis requires detailed tuned Monte Carlo.

Preliminary ~100-200 photons/ MeV for 1% WbLS.

Optimal optical coupling to photosensors in organic and noble liquids

Important new technical approach to collecting light using dichroic filters.

Basics of an etalon



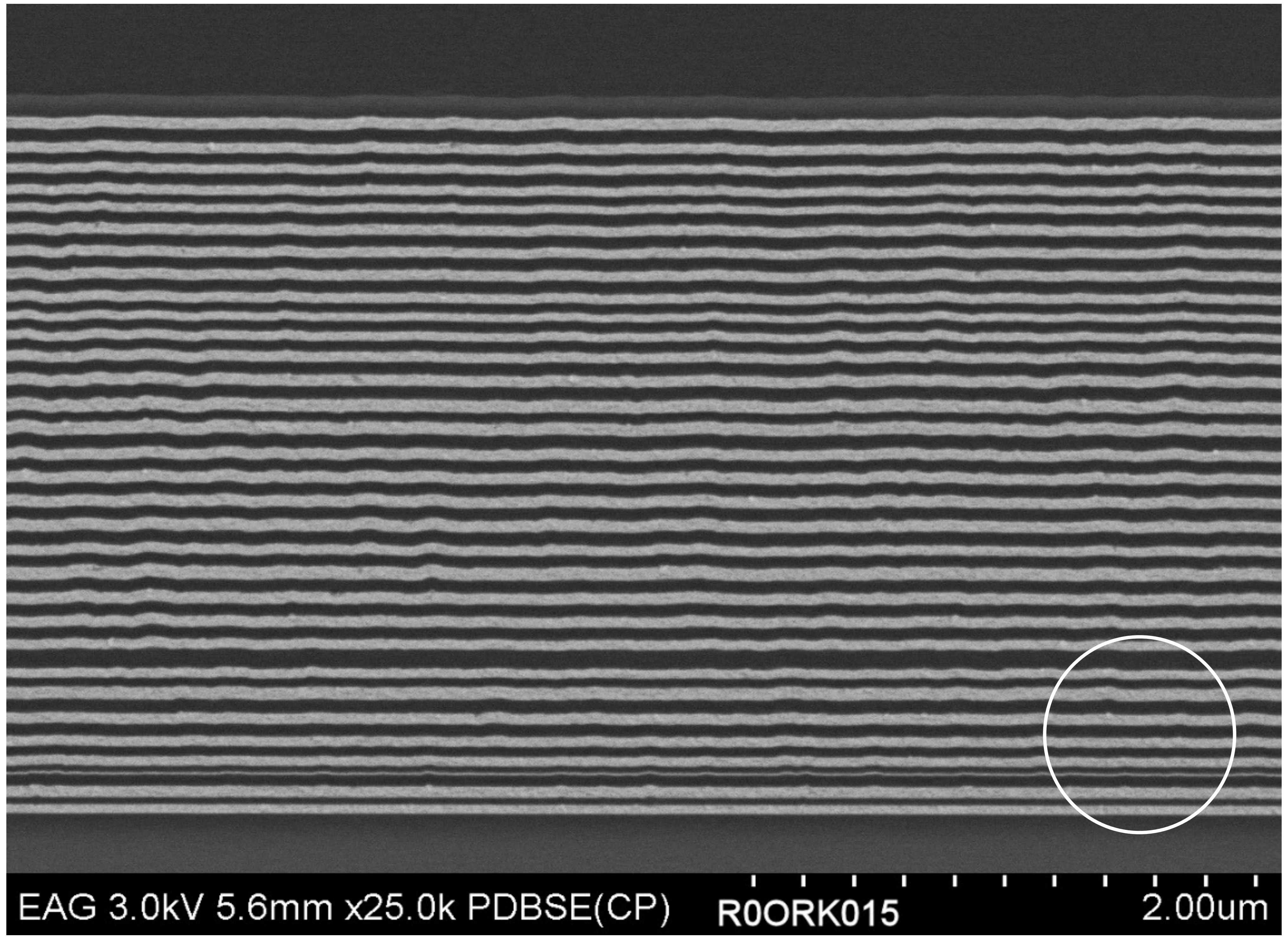
Moore, Coplan, Davis

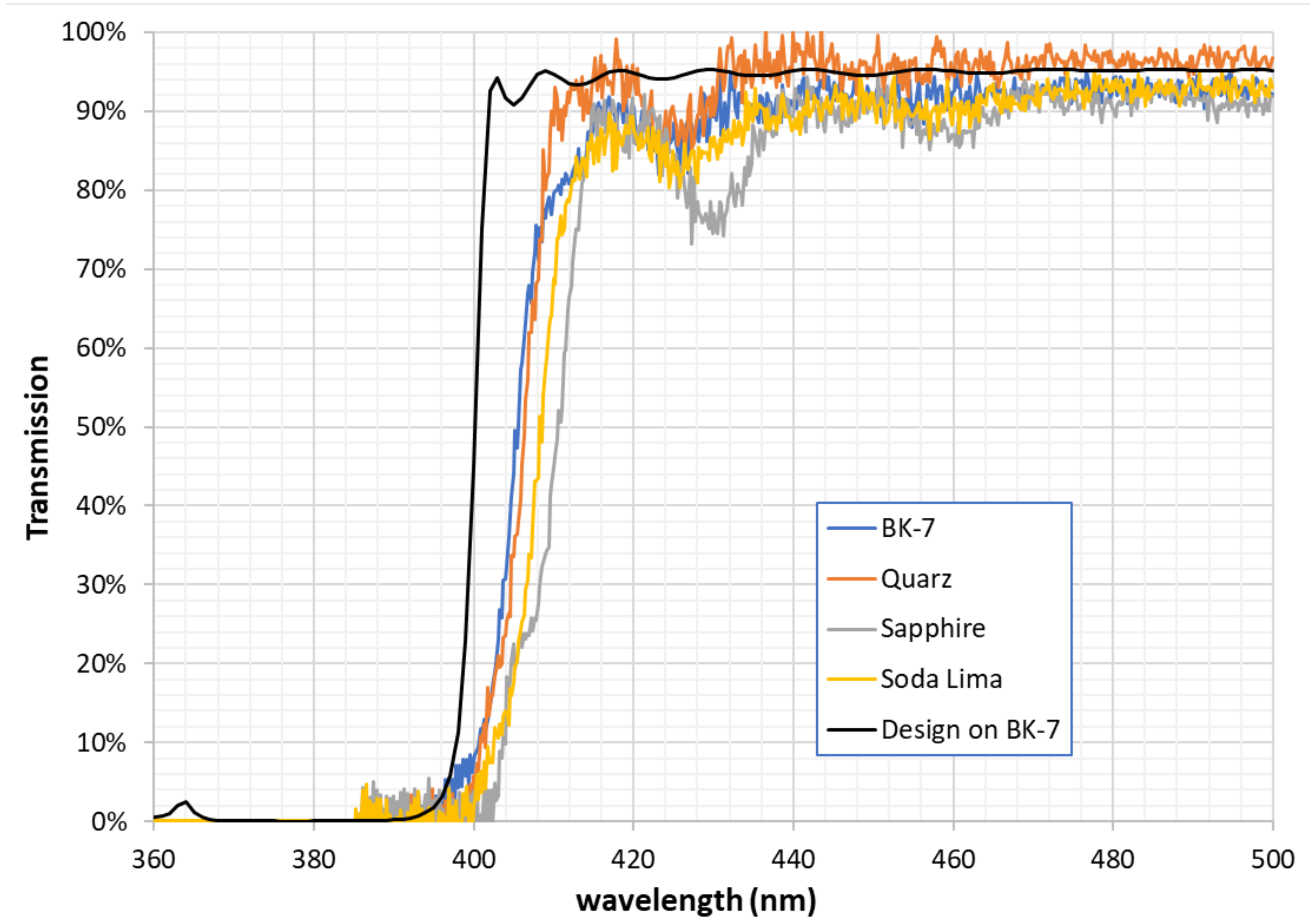
- If phase shift and absorption is neglected on interfaces.
- $\frac{I_T}{I_0} = \frac{1}{(1 + \frac{4R}{(1-R^2)}\sin^2\delta/2)}$ where R is the reflectivity and $\delta = 2kl\cos\theta$
- Transmission maxima happen when
- $l = \frac{m\lambda}{2\cos\theta}$
- A stack of etalons can be modeled by software to create a bandpass filter. Each etalon is made of a high quality dielectric layer with different index of refraction.

RAYTUM Photonics

Cross sectional SEM imaging of a full long pass Dichroic filter consisting of 64 total layers

Manufactured with the Atomic Layer Deposition technique





Measurements are calibrated by a standard sample, estimated measurement error (±1nm).

Dark band: dielectric material #1

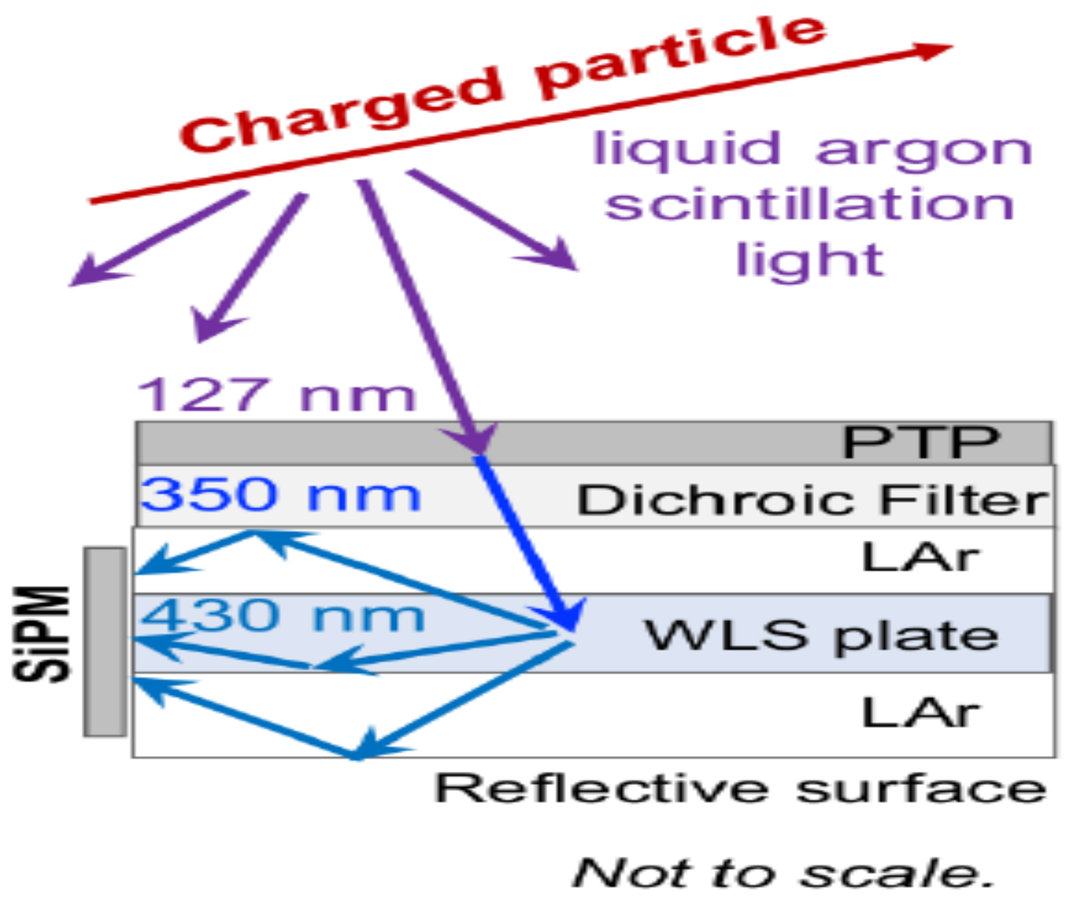
Light band: dielectric material #2

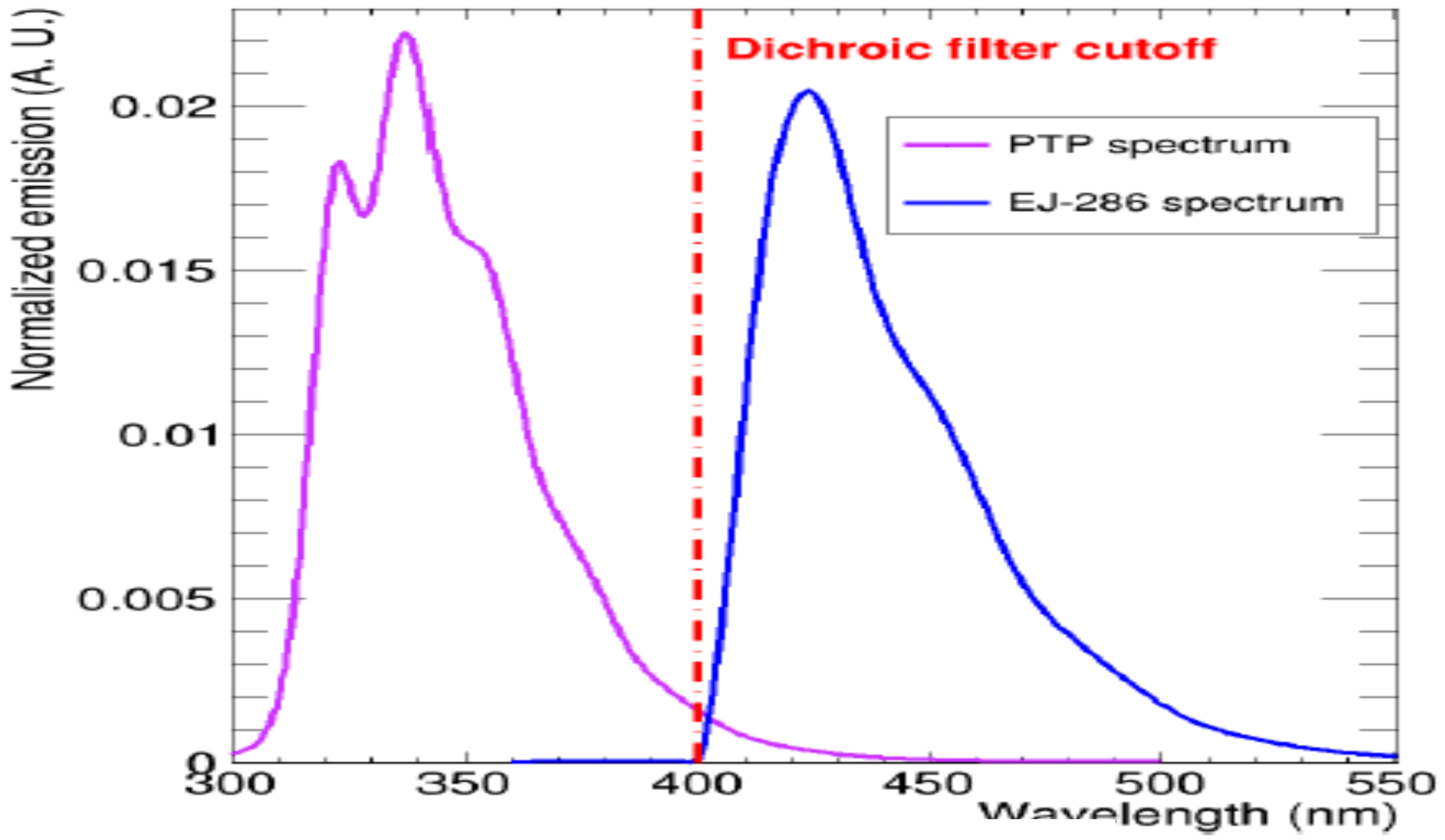
Measured performance in air at 0 deg on different substrates.

The edge will move with angle.

DUNE

Liquid Argon ARAPUCA detector concept and roles of DFs



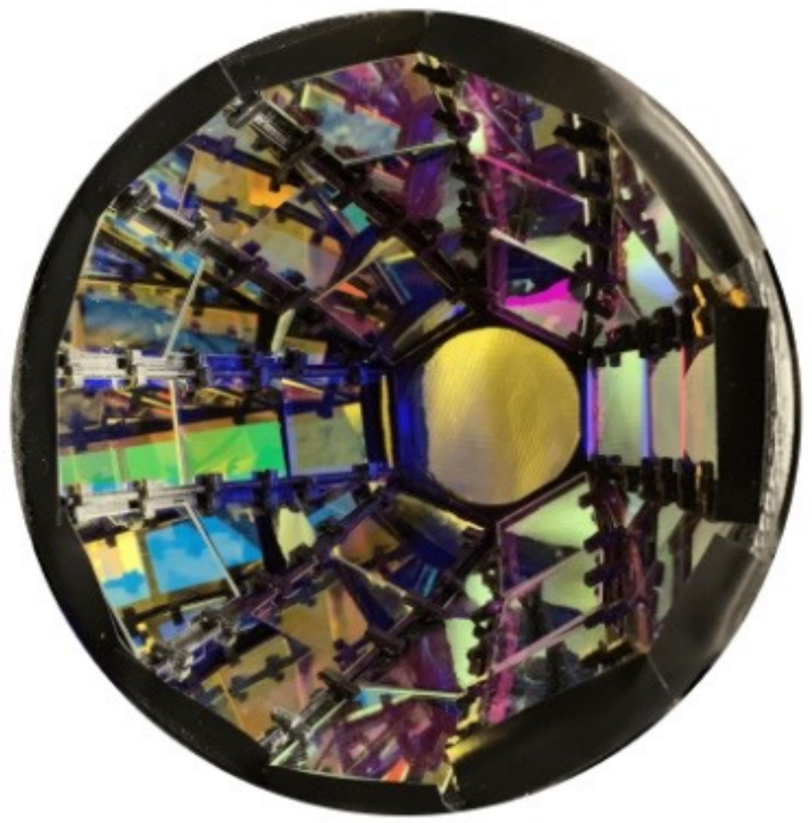


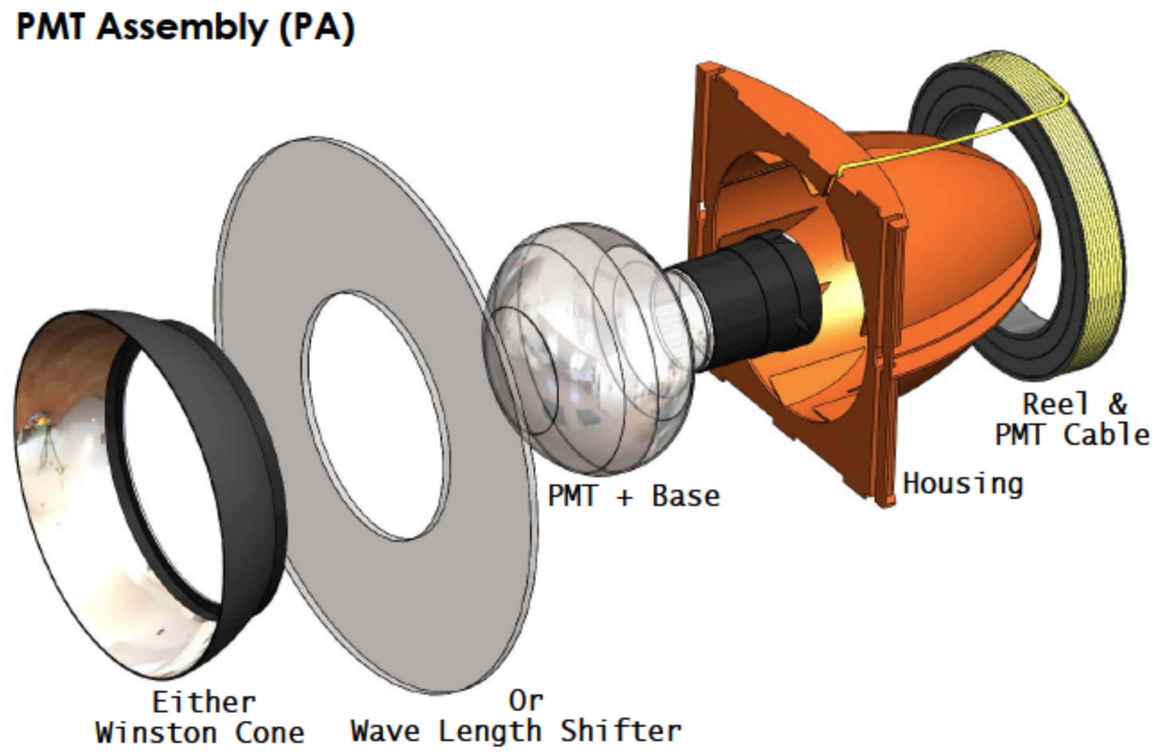
(Polymer EJ-286 WLSP)

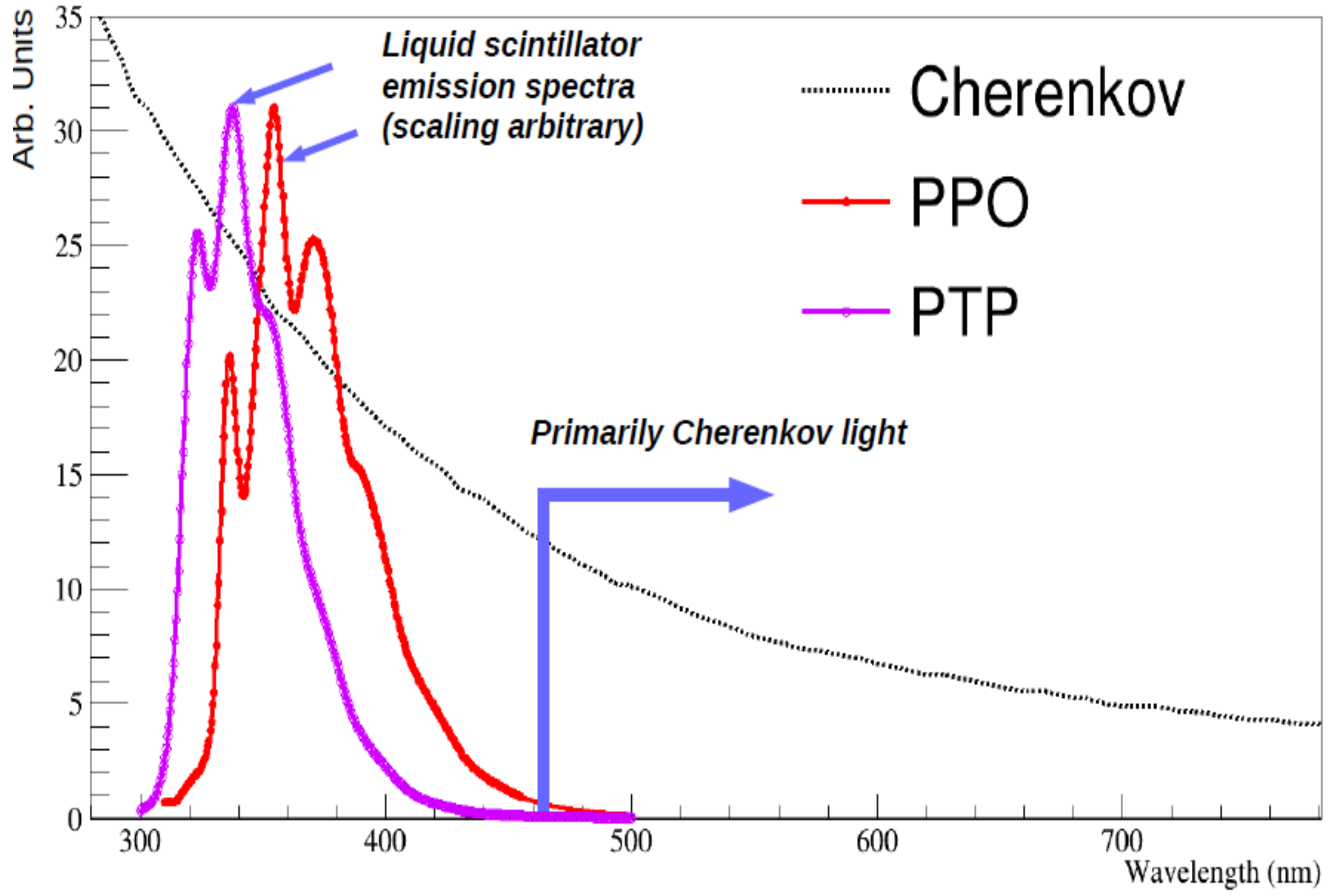
The dichroic cutoff (red dashed line), the PTP (purple) and the EJ-286 emission spectra. (b) X-ARAPUCA principle of work, with total internal reflection and the reflective cavity trapping photons.

THEIA

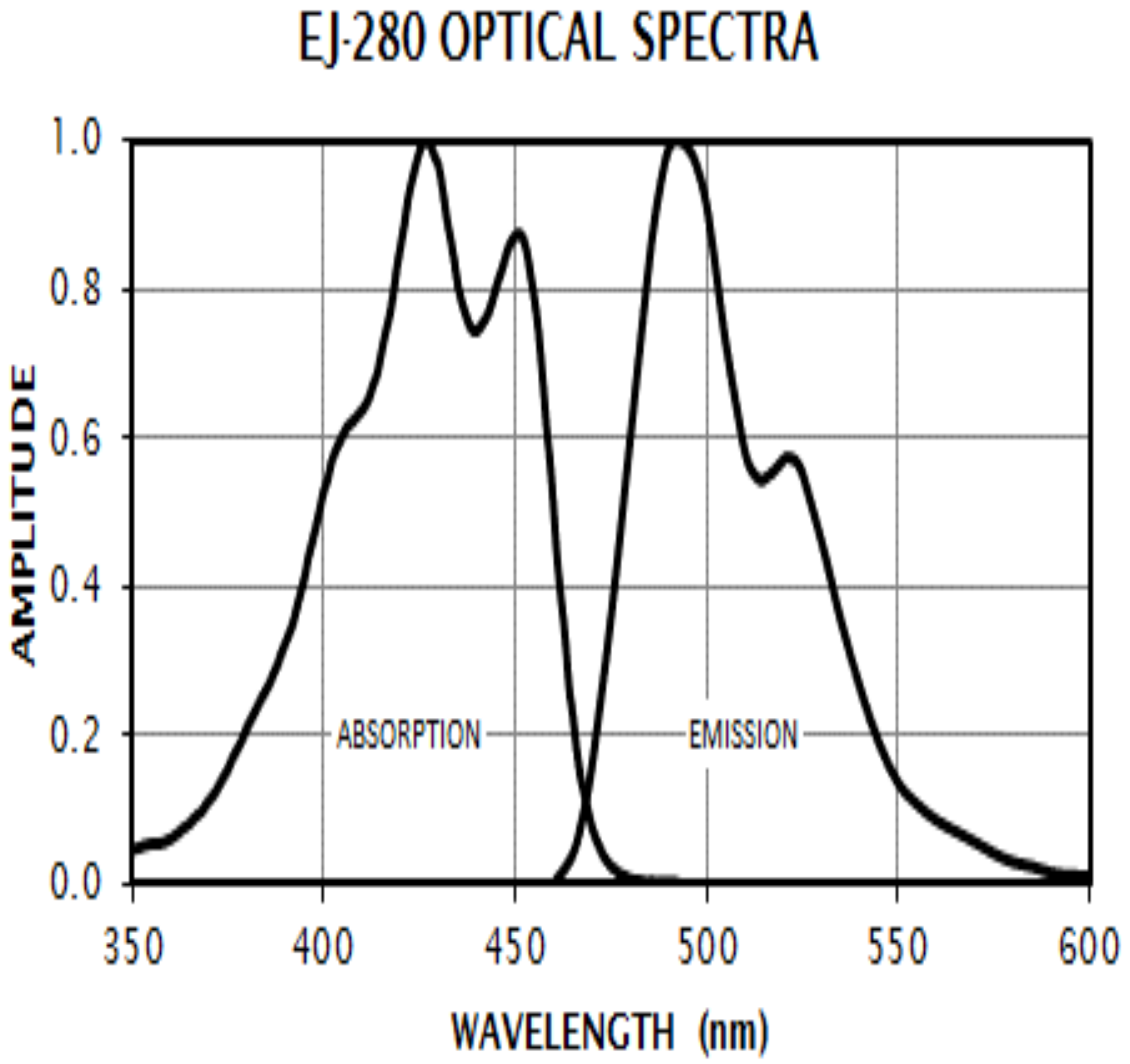
Winston cone(WC) /wavelength shifting plates(WLSP) type of detector concept and roles of DFS







Goal is to achieve Cherenkov and scintillation separation while losing as few total photons as possible.



The SP filters tile the barrel of the Winston cone and a central LP filter is placed at the aperture. A small amount of black electrical tape is used to block a small gap between the filters and the holder at the top of the dichroicon.

How does one deposit the layers ?

DUNE is using the PVD technique; but the state of the art is consider Atomic Layer Deposition.

- Precise and easy thickness control in a monolayer scale over established PVDs for high performance optical filter fabrication
- Conformity to non-planar geometries.
- Excellent uniformity (<0.1-1%) for fabricating large area optical components.

These systems are now becoming very large in industry and it is possible to coat many meter-squares in a few hours.

https://www.veeco.com/products/savannah-thermal-ald-for-rd/

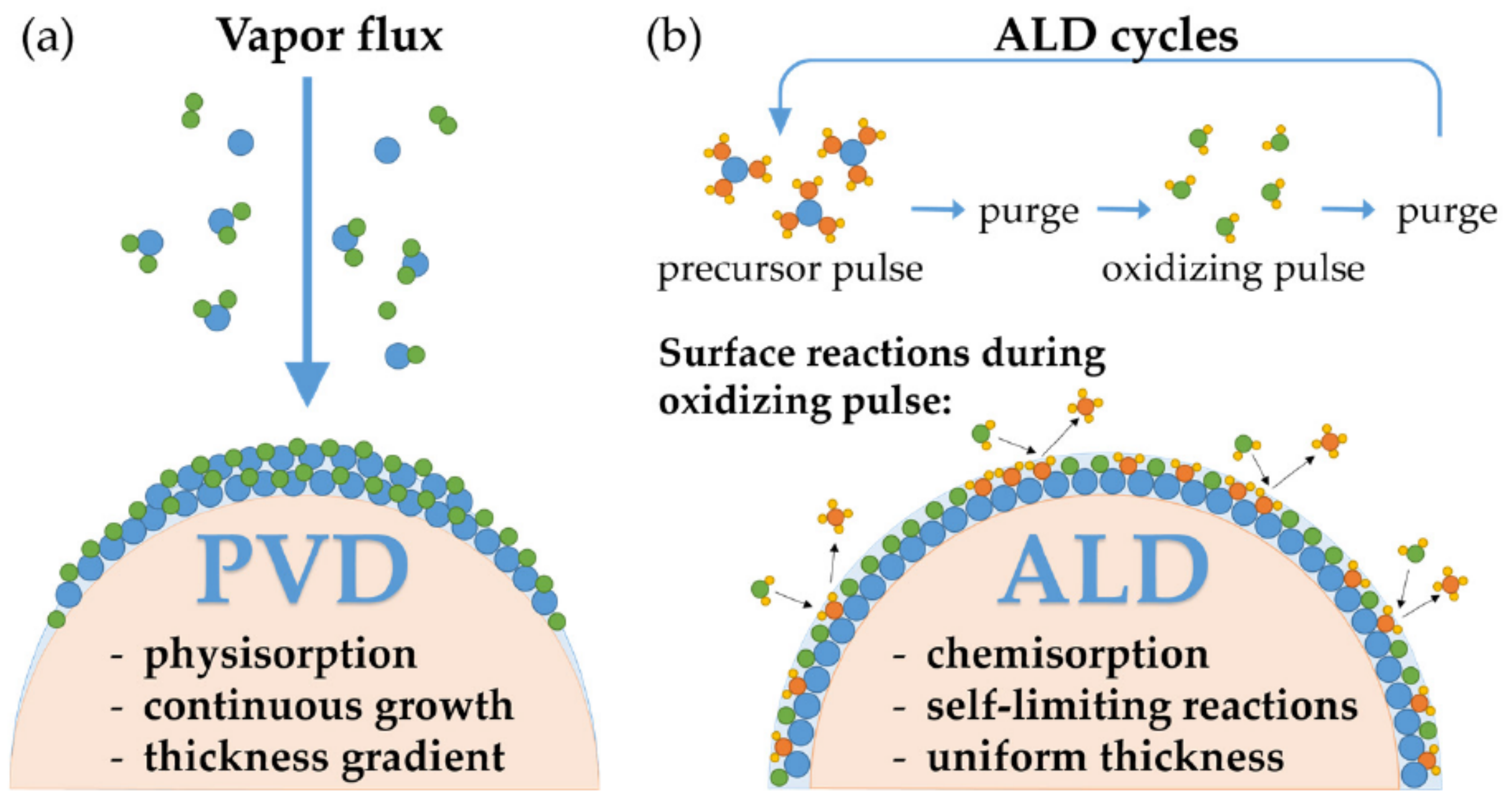


Figure 1. Illustration of (**a**) physical vapor deposition (PVD) deposition and (**b**) atomic layer deposition (ALD) on a hemispherical lens.

References

Not comprehensive; with some comments. A lot of material is available over the web through wikipedia and commercial references also.

Basics of molecular quantum states: Quantum Mechanics, Arno Bohn, 1979, Springer-Verlag, New York, Chapter III has detailed explanation of molecular vibrator-rotator model.

Regarding Jablonski diagram, Frank-Condon principle, Kasha rule: any modern course in molecular physics/chemistry.

Topical modern review of organic liquid scintillators: Metal-loaded organic scintillators for neutrino physics, Christian Buck, Minfang Yeh, 2016, J. Phys. G: Nucl. Part. Phys, 43, 093001. (Buck,Yeh (2016))

Review of modern approaches: Stefan Schoppmann, S*ymmetry* 2023, *15*(1), 11; https://doi.org/10.3390/sym15010011

Liquid argon scintillation review: E. Segreto, https://arxiv.org/pdf/2012.06527.pdf

Noble liquids: Noble gas detectors, Aprile, Bolotnikov, Bolozdynya, Doke. Wiley-VCH 2006.

For simulations in noble liquids: NEST: a comprehensive model for scintillation yield in liquid xenon, Szydagis, et al. JINST Vol 6, Oct 2011. https://arxiv.org/pdf/1106.1613.pdf

Regarding advanced microscopic simulations: Douglas, Penfold, Bezak, Computational and Mathematical Methods in Medicine, June 2015

Look for basic talks from Manfred Krammer, Bruce Leverington, Ken Hanson

Conclusion

State of the art

- Liquid scintillation technology and applications have reached new levels of scale and performance.
- New work on coupled scintillation materials that enhance signal, timing, and resolution and allows new capability
  - Water based liquid scintillators will provide scintillation media with longer attenuation lengths, larger scales, and Cherenkov/scintillation combined capability.
  - Liquid argon and Xenon combinations provides larger scales, better timing, and robust signal capability.
- New detectors
  - Massive new detectors are coming online. JUNO will be the largest organic scintillator detector, DUNE will be the largest noble scintillation detector.
  - New designs for DUNE phase II are emerging:
    - THEIA (water based liquid scintillator)
    - DUNE FD3/FD4 liquid argon will include much more capability for scintillation light.

Grand Challenges

- Is it possible to make more progress on software simulations with microscopic details on ionization energy loss and light production ?
  - Organic liquids with sufficient detail to model and predict optical performance.
  - In Noble liquids to provide greater understanding of coupled materials.
  - Are the software tools useful for detector design ?
- New imaging technologies to provide unprecedented event reconstruction and imaging.
  - Dichroic filters to sort wavelengths
  - Advanced cameras to image single photons
- New low cost higher performance windows for VUV light.