Tensor Enhanced Targets

An intensity sensitive endeavor

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Simple Principles For Online Evaluation

Monitor and Modify in Realtime

- Quick and easy bin by bin measurements after RF pulses (assuming high power limit)
  - ***Differential binning:***
    - Breaks things up into NMR bins for fast and easy interpretation.
  - ***Rates response:***
    - For RF driven part, implies $A_{loss} = 2A_{gain}$ under high RF power limit.
  - ***Spin Temperature Consistency:***
    - Just for the hole, but assumes nothing much is changing in the other part of the line.

Polarization mechanism and diffusion model Independent

Comments from Previous Reviews

And what we *think* we are doing

- **Does the line deform due to complicated spin diffusion that prevents us from accurately measuring the polarization?**
    - The mechanisms to depolarize (with hole burning in the high power limit) and flip with AFP are well understood. Spin diffusion does not play a leading role in these mechanisms in the proper setup.
    - Can we prove this: yes, mathematically, but accurate measurements of spin diffusion in the spin-1 system is complicated especially in CW-NMR (but not impossible).
    - What about spectral diffusion with/without microwaves, how does it contribute: This is a big part of recovery after manipulation, but nothing unexpected seen in before and immediately after comparisons. However, system continues to evolve and spectral diffusion dominates in filling in the hole.
- **Why was TRIUMF not successful experimentally in enhancing and measuring tensor polarization (note)?**
    - Within error it seems that they were successful, but the error was pretty large.
    - We do not believe TRIUMF had reliable lineshape theory in hand or good control of NMR related errors.
- **Have we demonstrated high enough tensor polarization in experimental conditions?**
    - During the conditional review we demonstrated reliable enhancement and measurements of over 30% tensor polarization but the question remained if this met the ***experimental conditions*** requirement.
    - ***Experimental conditions*** seemed to be defined as using cold irradiated ND3 rather than d-butonal. We can prove that the lineshape theory for this equivalence holds in the high power limit. What other demonstration is needed if cold irradiated ND3 does not become available? What other criteria does demonstration of ***experimental conditions*** pertain to?
    - Do we need to focus on higher polarization rather than optimized running as described in the previous review?
    - We have already demonstrated alternating sequences improve the figure of merit as compared to the original proposal, is this our goal rather than meeting a particular high-water mark?

Understanding Rate Response + STC

Recall - No spin diffusion terms in the high RF power limit

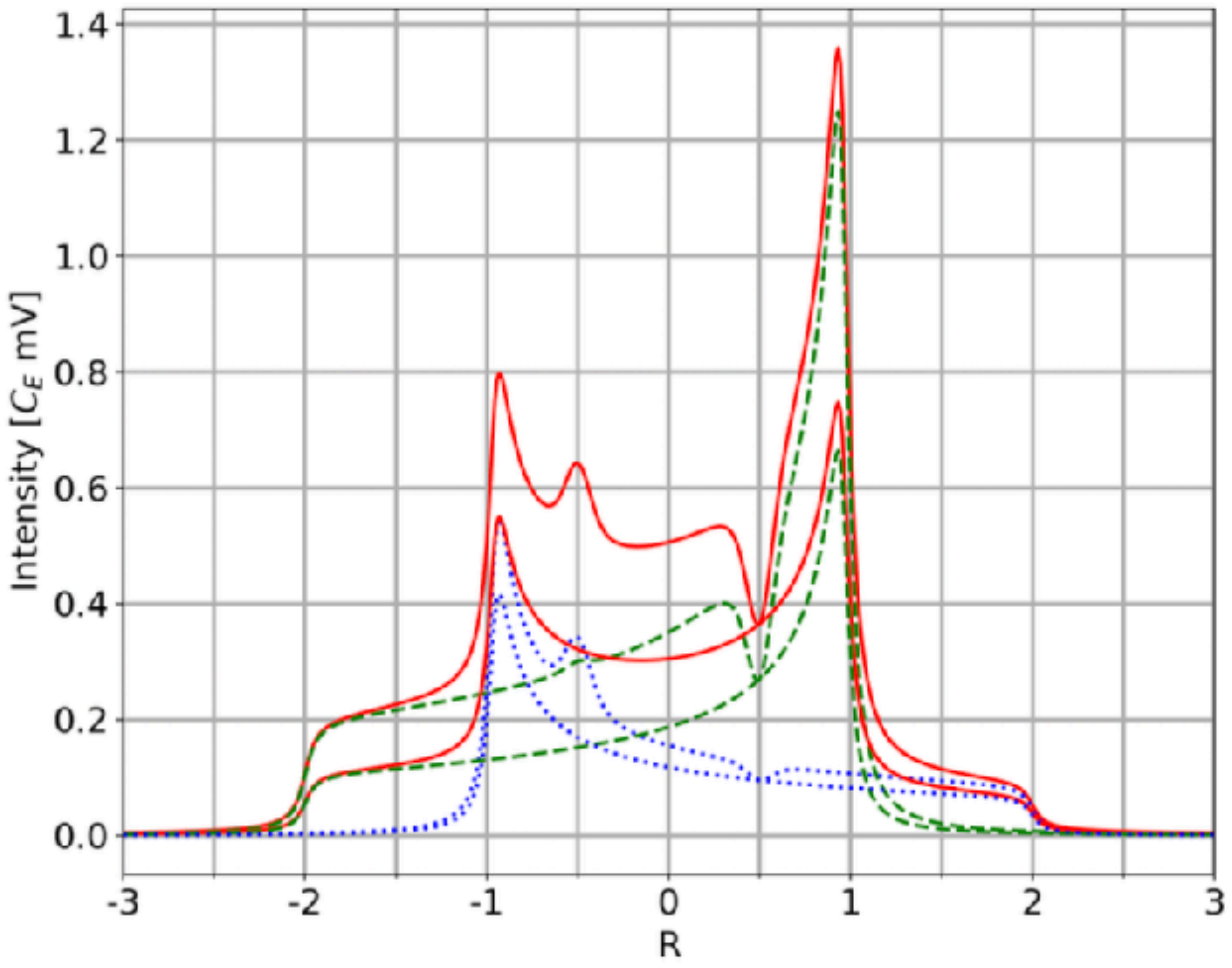
$$
\begin{aligned}
I_+^f &= C\left[(\rho_+ - \xi\rho_+) - (\rho_0 + \xi\rho_+)\right] \\
I_+^f &= C\left[(\rho_+ - \rho_0) - (2\xi\rho_+)\right] \\
&\implies \dot{I}_+^i(-\mathcal{R}) = -2C\xi\rho_+.
\end{aligned}
$$

$$
\begin{aligned}
I_-^f &= C\left[(\rho_0 + \xi\rho_+) - (\rho_-)\right] \\
I_-^f &= C\left[(\rho_0 - \rho_-) + (\xi\rho_+)\right] \\
&\implies \dot{I}_-^i(\mathcal{R}) = +C\xi\rho_+.
\end{aligned}
$$

$$
\begin{aligned}
\dot{I}_+(\mathcal{R}) &= -\frac{1}{2}\dot{I}_-(-\mathcal{R}) \\
\dot{I}_-(\mathcal{R}) &= -\frac{1}{2}\dot{I}_+(-\mathcal{R}).
\end{aligned}
\qquad A_{gained} = \frac{1}{2}A_{lost}.
$$

$$
\begin{aligned}
\frac{dn_{+1}}{dt} &= -W_{+1\to 0}n_{+1} + W_{0\to +1}n_0 + D(n_{+1}^{\text{eq}} - n_{+1}), \\
\frac{dn_0}{dt} &= -W_{0\to +1}n_0 - W_{0\to -1}n_0 + W_{+1\to 0}n_{+1} \\
&\quad + W_{-1\to 0}n_{-1} + D(n_0^{\text{eq}} - n_0), \\
\frac{dn_{-1}}{dt} &= -W_{-1\to 0}n_{-1} + W_{0\to -1}n_0 + D(n_{-1}^{\text{eq}} - n_{-1}).
\end{aligned}
$$

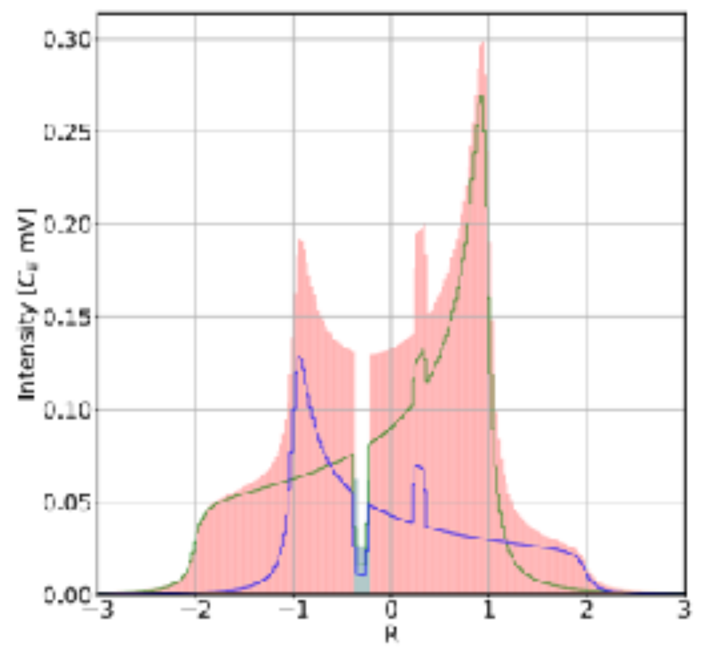
$$
\begin{aligned}
\frac{dn_{+1}(\theta_0)}{dt} &= -W_{+1\to 0}n_{+1} + W_{0\to +1}n_0 - R(n_{+1} - n_0) \\
&\quad + D(n_{+1}^{\text{eq}} - n_{+1}), \\
\frac{dn_0(\theta_0)}{dt} &= -W_{0\to +1}n_0 - W_{0\to -1}n_0 + W_{+1\to 0}n_{+1} \\
&\quad + W_{-1\to 0}n_{-1} + R(n_{+1} - n_0) + D(n_0^{\text{eq}} - n_0), \\
\frac{dn_{-1}(\theta_0)}{dt} &= -W_{-1\to 0}n_{-1} + W_{0\to -1}n_0 \\
&\quad + D(n_{-1}^{\text{eq}} - n_{-1}).
\end{aligned}
$$

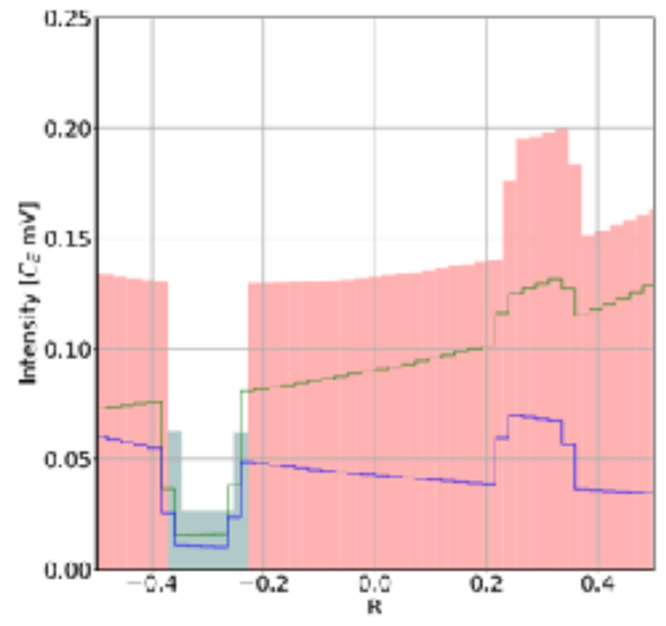


- We can get away with ignoring spin diffusion (R>>D)
  - Microwaves also increase D (microwave driven transitions)
  - Easier to turn off microwaves to measure, then D is very small
  - For experimental testing: Need RF amp and high Q, need error really well quantified, and need to measure as soon as possible before mixing

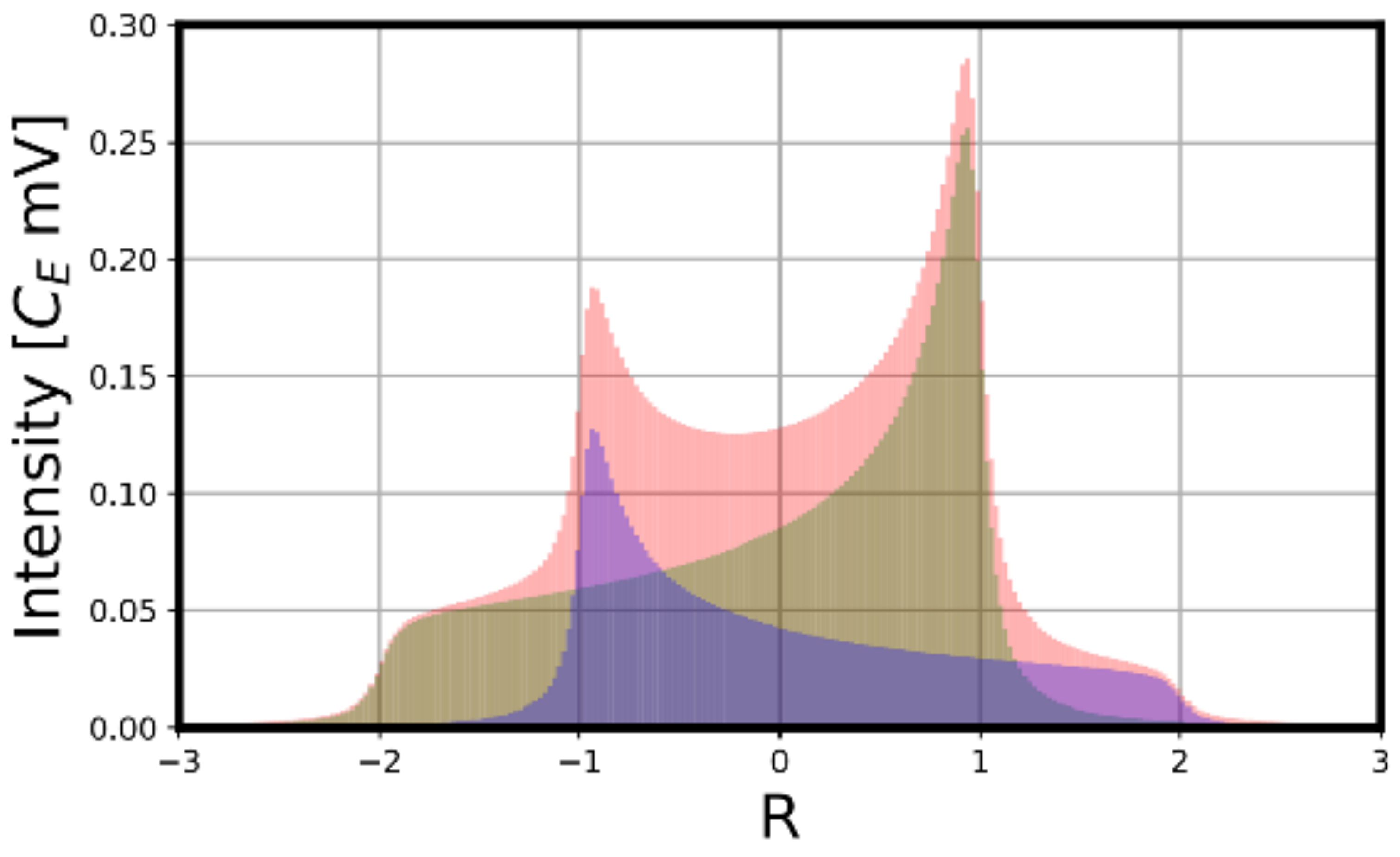
Putting it all Together

Without realtime evolution





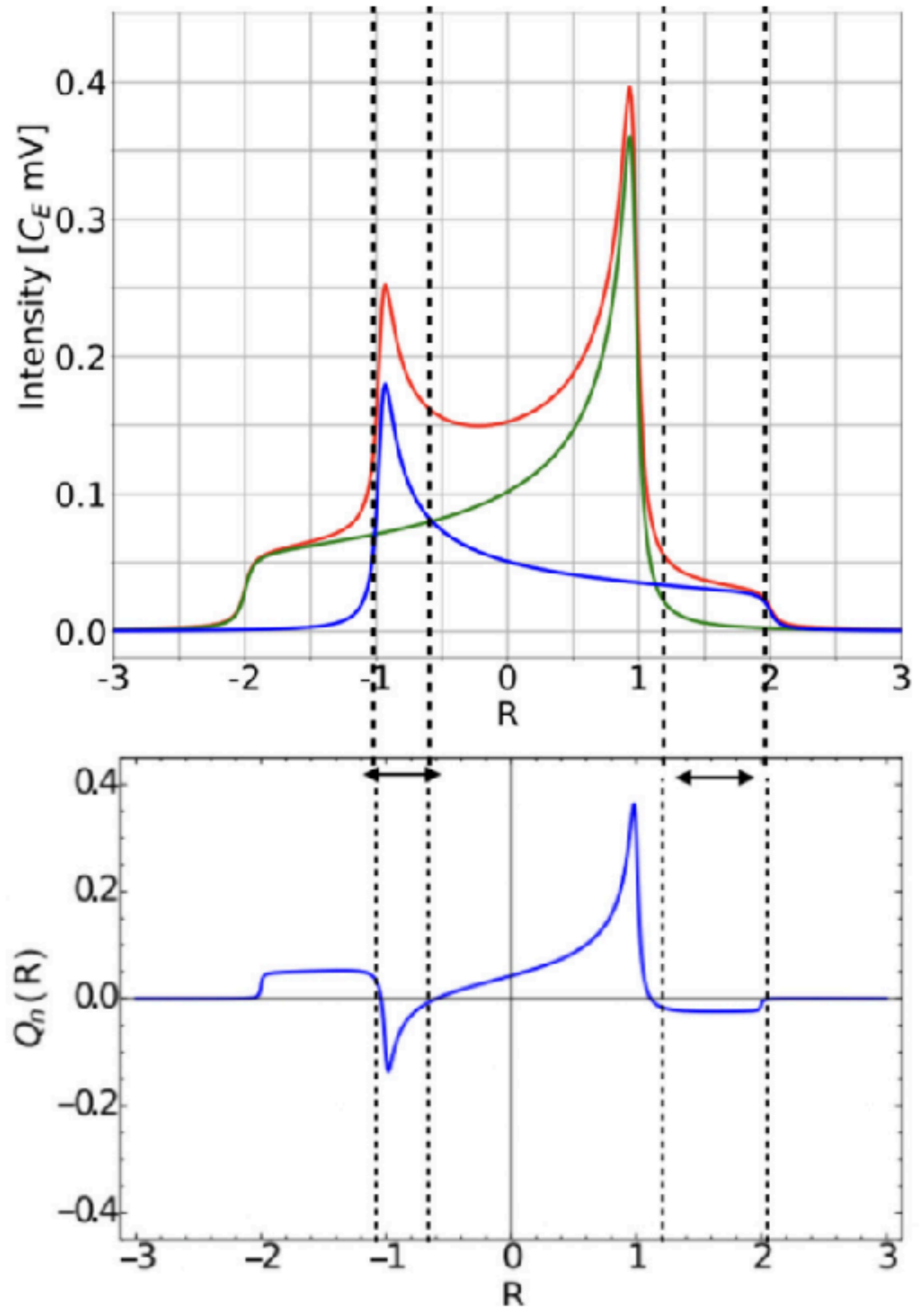
- Differential binning with all the tricks in place
  - Calibrate to interpret differential areas.
  - RR, STC, DB leads to very simplistic bookkeeping to monitor polarization by indexing bin +/- area.
  - Assumes application of power sensitive pulses.
  - High power, short pulses, narrow width (for shaping).
  - So best measurement, immediately after pulse.
  - Cannot (by itself) be used to evolve signal.



Experimental Running

Assuming low budget option (but many other possibilities)

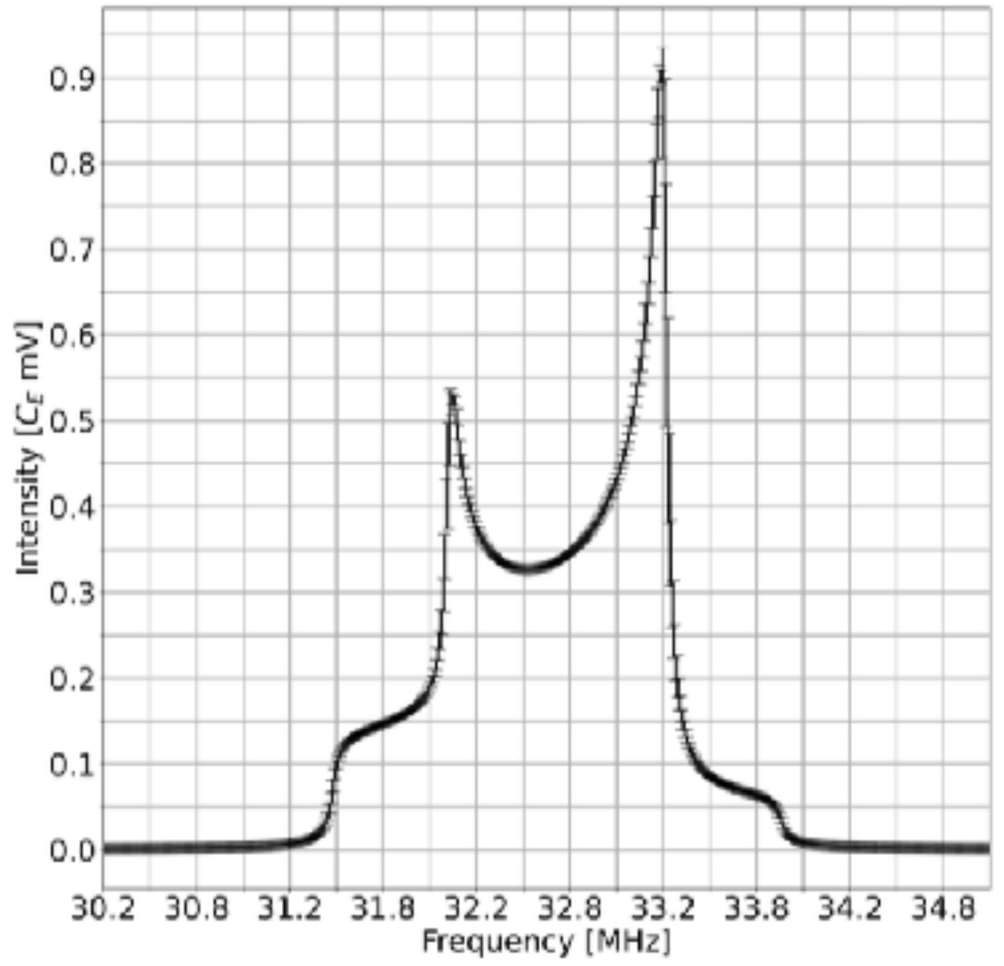
- Protect NMR.
- Apply ss-RF as a function of power profile defined by Q(R) in the sweep pulses in the high power limit using the AFP coil rather than specialized NMR.
- Have fast DAQ to do high averaging of many sweeps quickly.
- Update sequence per bin and power profile as system evolves under DNP and radiation damage.
- Whats needed: Optimized coil (for both AFP and ss-RF), amplifier, generator, maybe upgrade to NMR DAQ, automated software to adaptively control power profile and pulse sequences.

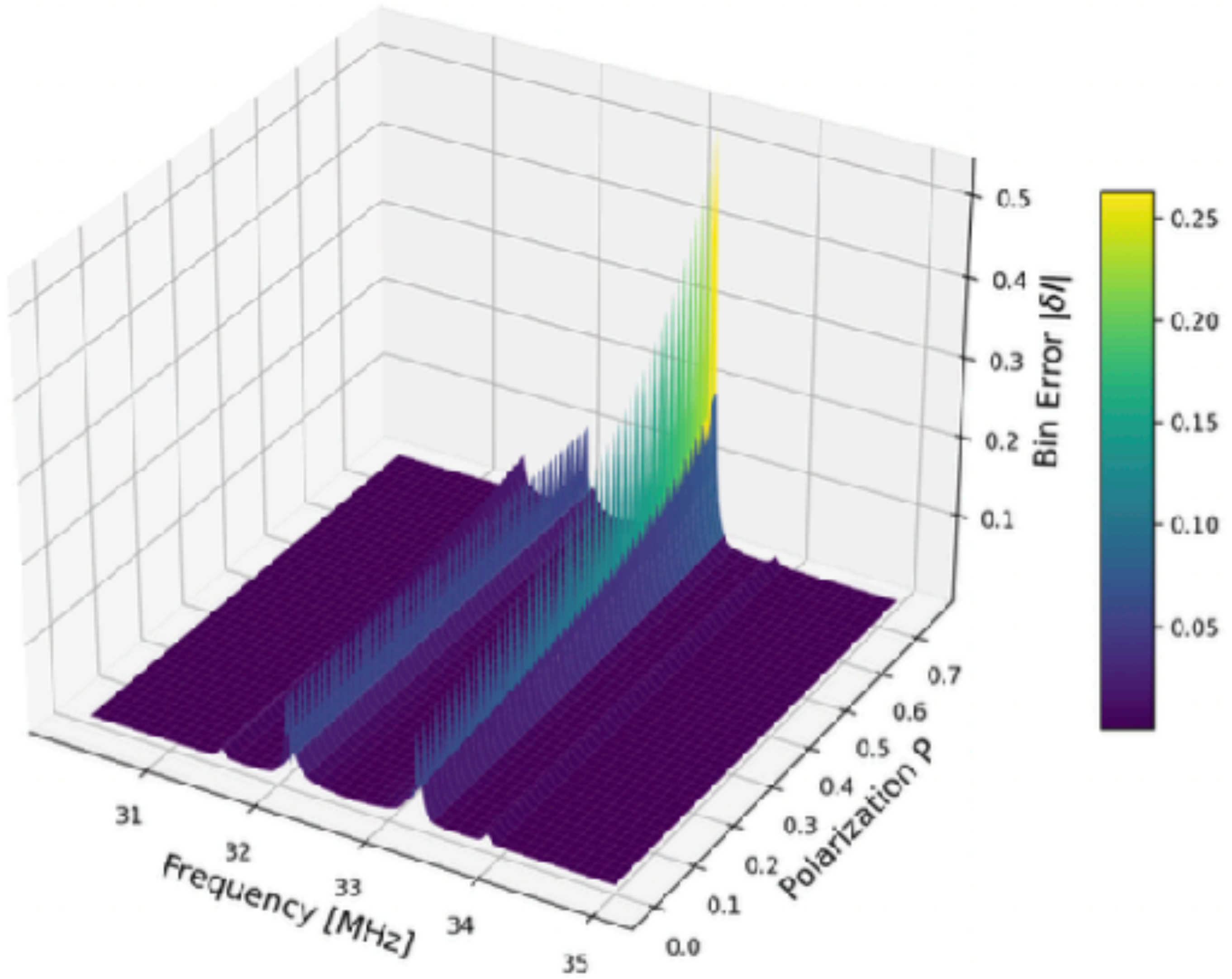


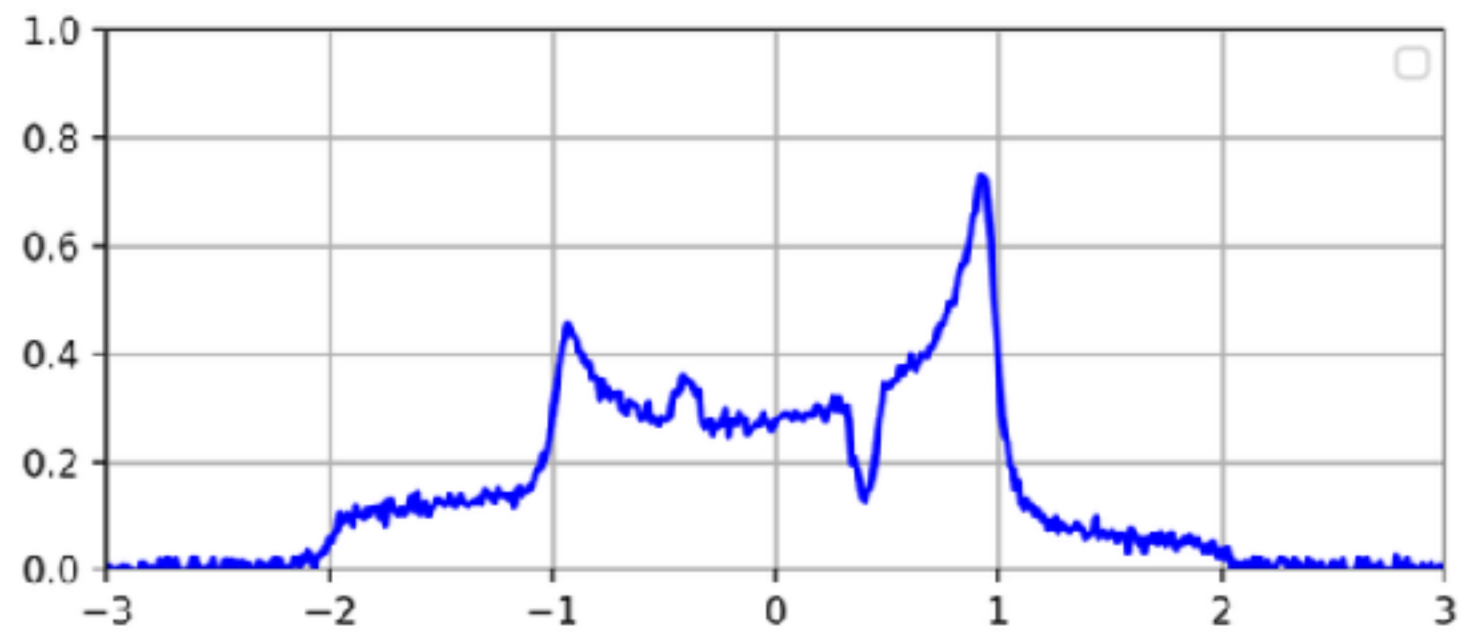
How To Make Sense out of NMR data

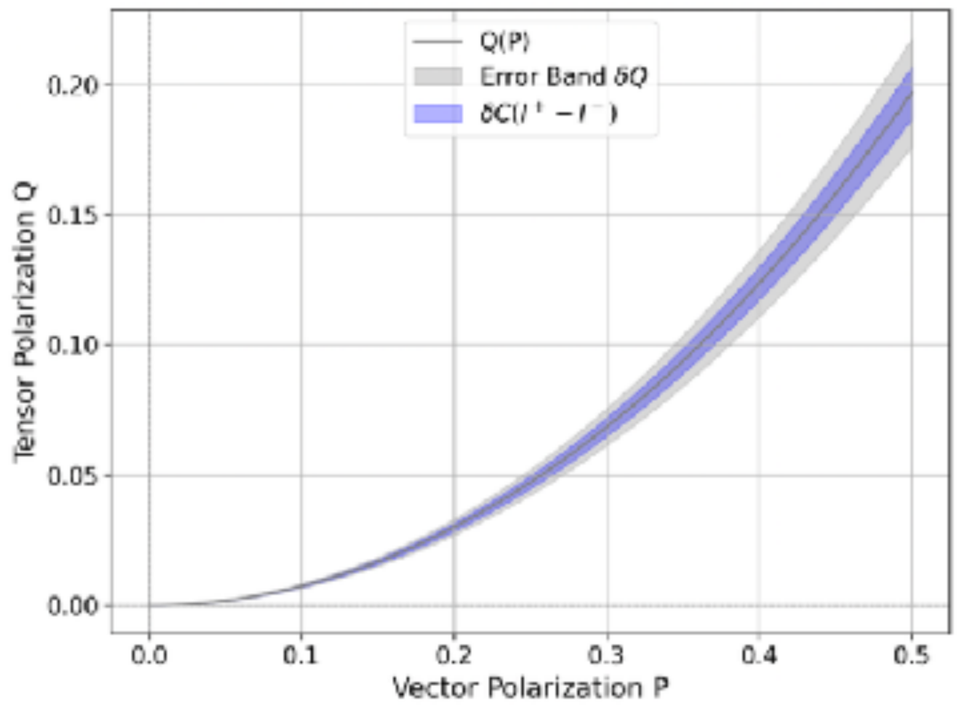
Error specific to ss-RF

- Bin Error (from differential binning)
- Changes in signal during NMR (sensitive to number of sweeps)
- Averaging (over sweeps) uncertainty
- Standard RF noise: Gaussian, sinusoidal, baseline shifts,
- Errors in characterization of initial line (area calibrations)





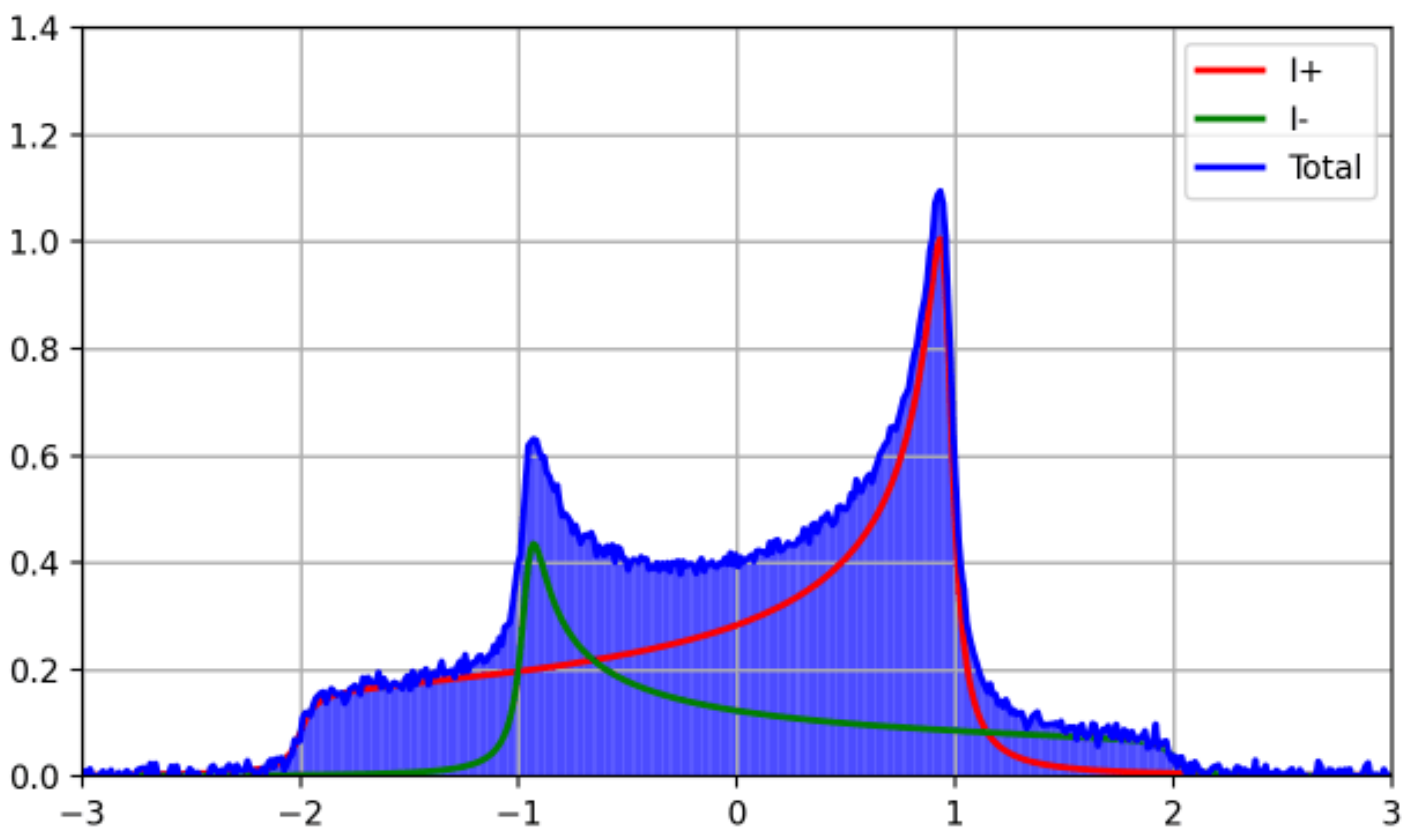


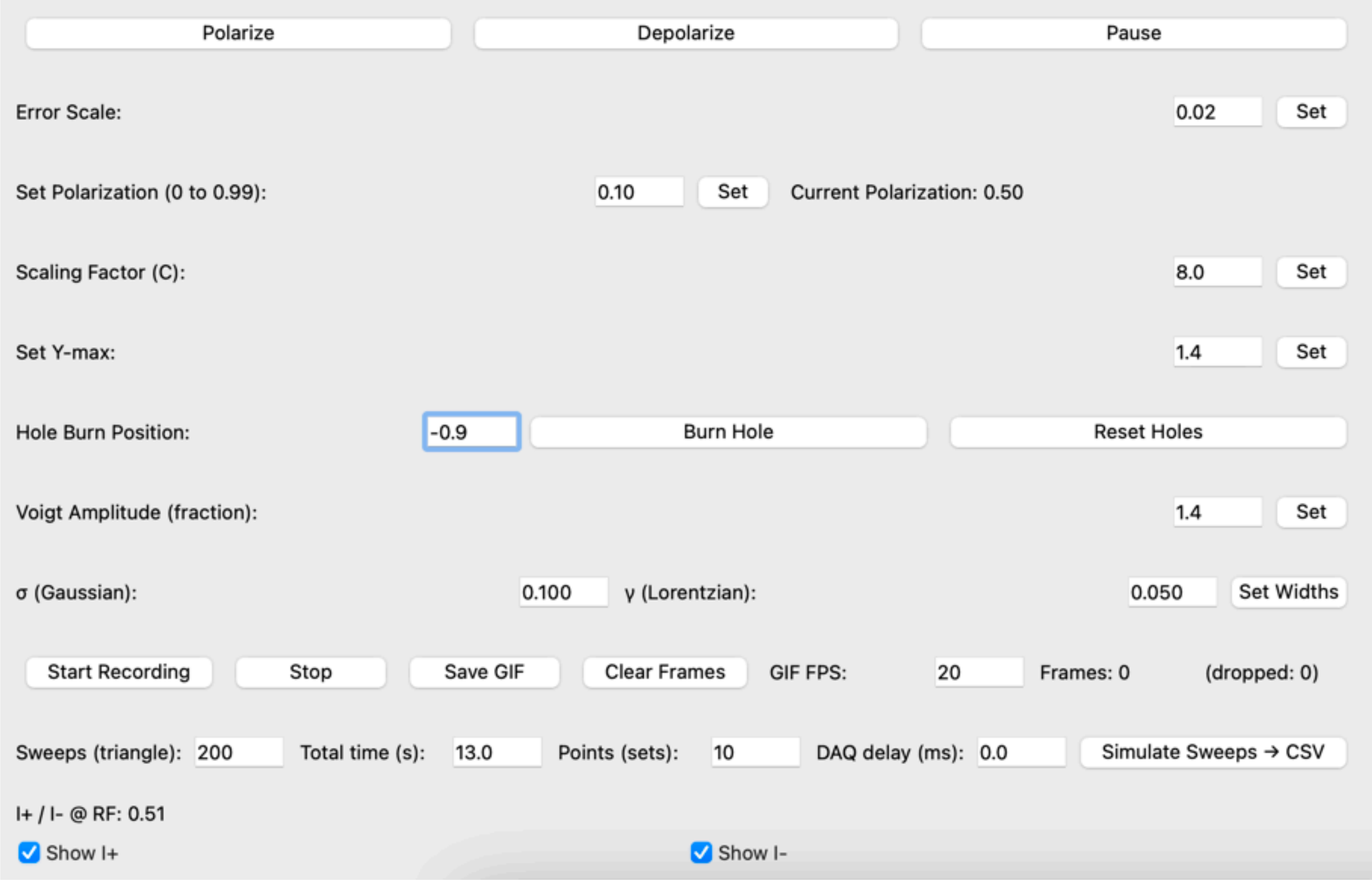


Realtime Simulations

With simulated sweep rate and DAQ time

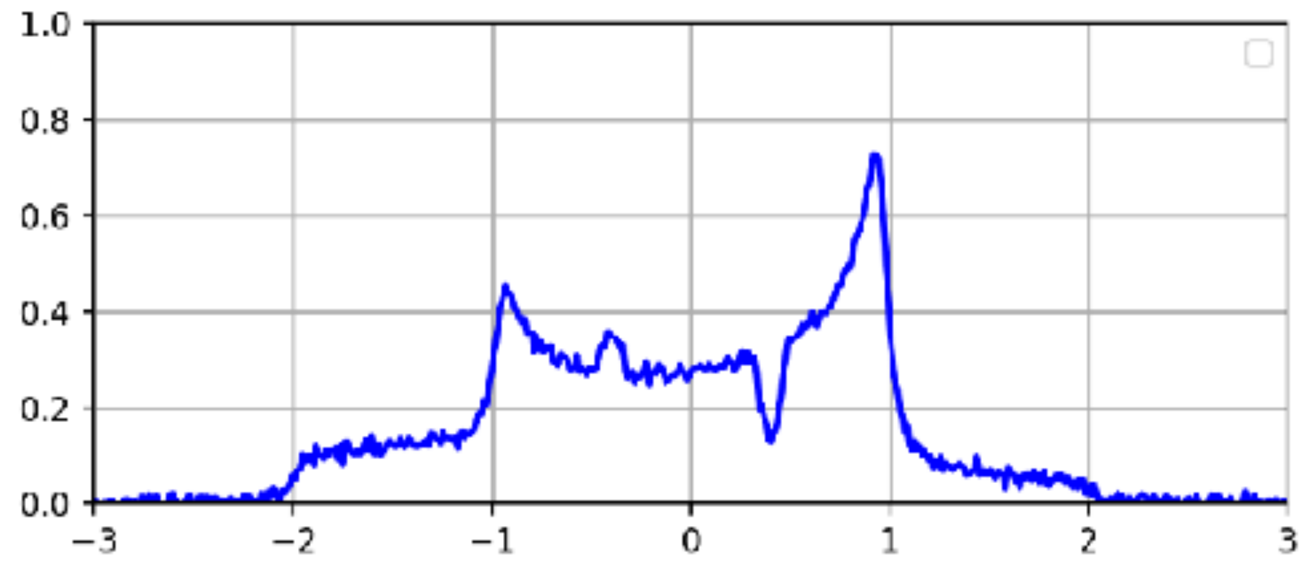
- Needed to evaluate errors associated with loss of information during system evolution.





Quantifying Uncertainties

From the ss-RF contributions



- Ensure proper setup (instrumentation)
    - Need High RF power, highly tuned coil, and high fidelity timing control
- Ensure proper setup with respect to error estimates (MC)
    - Need to model the acquisition and sampling delays
    - Realtime simulations (accuracy and precision)
- Quantify measurement errors
    - Uncertainty studies of the standard and ss-RF associated error so we know how meaningful the measurements are
- Calibrate multiple ways and reduce start point errors

Source (Type)	**Mechanism / scaling**	**Dominating when**
Sampling Delay (Type A)	$\mathcal{O}(t_{\text{acq}}/\tau_{\text{dyn}})$	acquisition latency is large
Bin Error (Type B)	$\mathcal{O}((\Delta f/\Gamma)^2)$	large bin size
Asymmetry vs area (Type C)	$(dP/P < 1\%)$	calibration limitations
Non–Boltz. spin-temp breakdown (Type D)	$(dP/P < 1\%)$	Inhomogeneous microwaves
Modeling Error) (Type E)	$\mathcal{O}((B_{RF}/B_\mu)^2)$ $\mathcal{O}(\mathcal{R}/D)$	Low RF power; long fixed burns

What is required?

How to prepare for (target part of) ERR

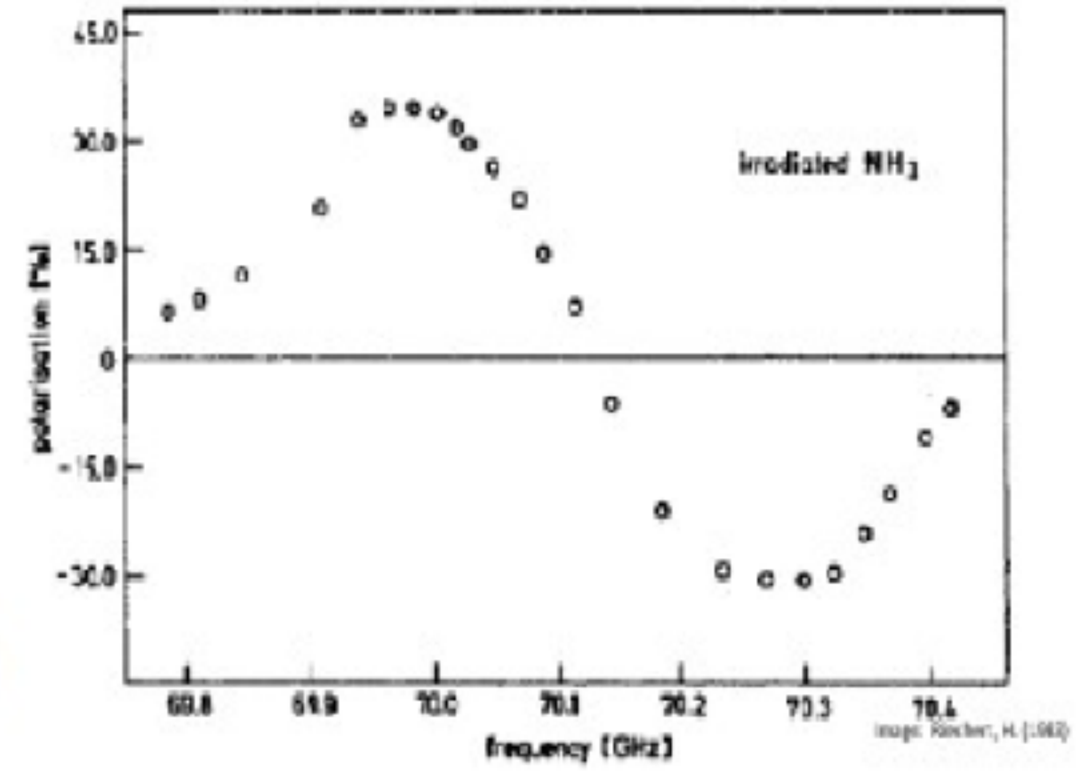
- Do we need to have and test cold irradiate ND3? (Might have some now, but not sure)
- Do we need to understand cold irradiated ND3 in great detail or just show an equivalence?
- Do we need to fully characterize spin diffusion (with and without DNP)?
- Do we need a to reach a higher benchmark for tensor polarization under certain conditions?
- Do we need to prove with scattering data that modern lineshape theory is correct?
- Focus on run configuration and overall FOM?
- *ss-RF hardware (easy setup vs optimal setup)*
- *AFP (and coil configuration) optimized for our field orientation*

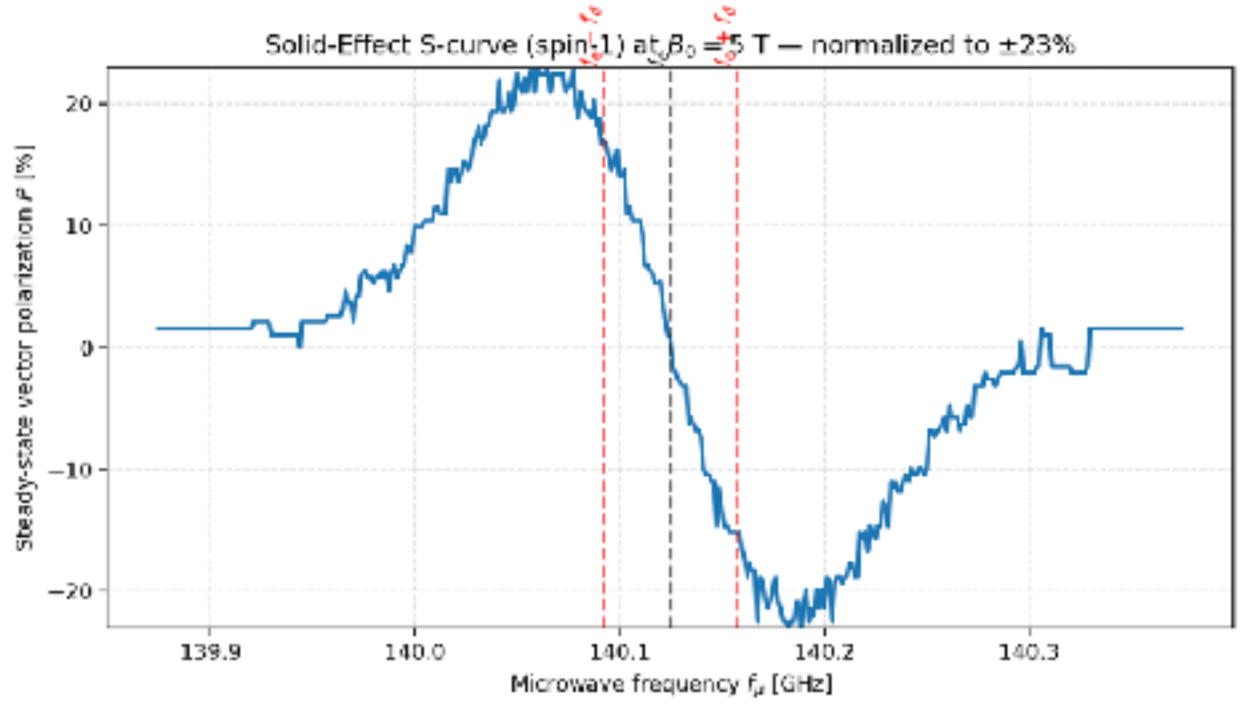
Understanding ND3

- Are there questions about lineshape differences d-butanol and ND3 equivalence?
- Do we just need some in hand to do the same thing done with d-but as a benchmark?
- Do we need to understand the rate equations for each (ND3/d-but) to prove that the differences in evolution do not change the max Pzz?
  - What we know is diffusion and relaxation pathways are similar but at very different rates.
  - T1 and hole filling are much slower for ND3 but this does not change equivalence in the lineshape only in recovery time. This was already studied in warm irradiated ND3 several years back (also new tests from UNH).

Understanding ND3

- Getting rate equations tuned and optimized then experimentally parameterized then again tested with projections and experimental verification
  - **Just my opinion**: This is not trivial. Realistic rate equations for all dose conditions are complicated and ND3 is uniquely complicated. Still fun to pursue but this should not be part of our first line of defense.
  - **How to do it**: Lots of spin up data for various microwave and dose states in various phases of target lifecycle as well as many T1s from decays (and ideally T2 and hole recovery theta mapping).
    - Obtain S-curves for dose conditions
    - Determine best candidate beyond ND2 for low temp radical
    - Some candidates: trapped atomic deuterium (D• from $ND_3 \rightarrow ND_2• + D•$), or ND_3^+ from $ND_3 + h+ \rightarrow ND_3^+$ where we can study these types of things without measuring ESR using computational tools. But some ESR type info would be needed to properly simulate





- **Radical concentration** c_e: rates scale *linearly* with c_e because the SE is mediated locally at paramagnetic sites.
- **Electron relaxation**: T_{2e} enters the numerator (transition probability per unit time) and the detuning denominator; T_{1e} enters via the saturation product $T_{1e}T_{2e}$.
- **ESR width** Δ_e: appears through the packet weight L_e; when $\Delta_e \ll \omega_d$ one recovers the narrow–line limit assumed by Fedders & Souers for analytic simplicity. [3, Sec. II].
- **Microwave field** B_1: enters as $\omega_{1e}^2 = (\gamma_e B_1)^2$.
- **Hyperfine distribution**: $\langle A_\perp^2 \rangle$ collects the r^{-6} dipolar tail and site geometry; it is a single fit parameter at fixed radical and matrix.

Characterize Spin Diffusion

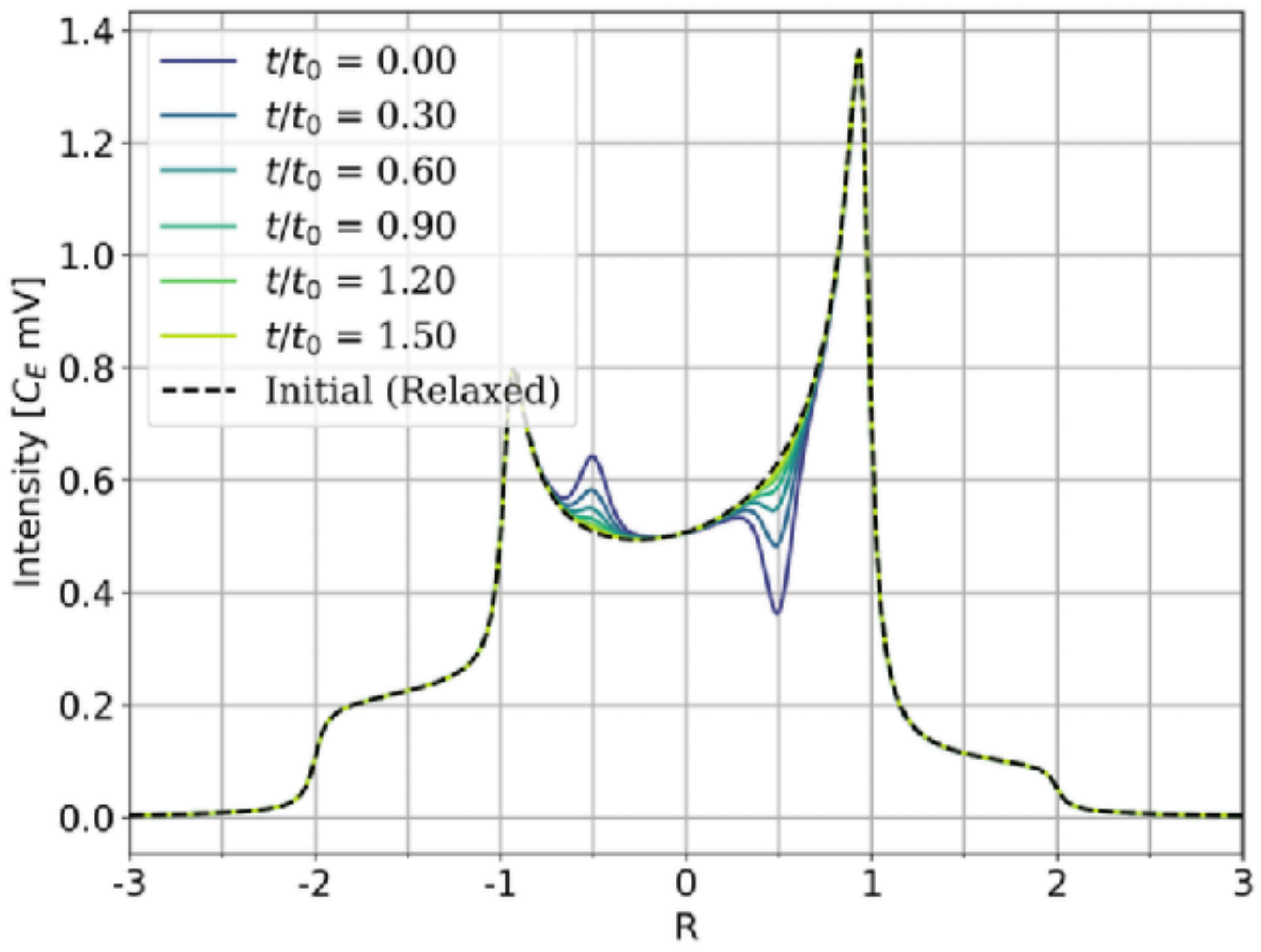
With and without DNP

- Assume diffusion changes not only as a function of intensity but also the angle.
- Then map out from measurements at different intensity and angle to quantify.
- Stick it in the expression and test by predicting recovery under not measured scenarios.

$$\frac{dn_i(\theta_0, \vec{r})}{dt} \supset D[n_i(\theta_0, \vec{r})]\nabla^2 n_i(\theta_0, \vec{r})$$

the variable θ_0 labels a *fixed subset of spins* whose internuclear (or EFG) axis makes an angle θ_0 with the external field.

The diffusion operator ∇^2 here acts in **real space** (the spatial coordinate $\vec{r}$), describing **spatial spin diffusion** — i.e. polarization exchange between nearby sites in the material through dipolar flip-flop processes.



Continuum Laplace–Beltrami form

$$\left(\frac{\partial n_i}{\partial t}\right)_{\text{diff}} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(D(\theta)\sin\theta\frac{\partial n_i}{\partial\theta}\right)$$

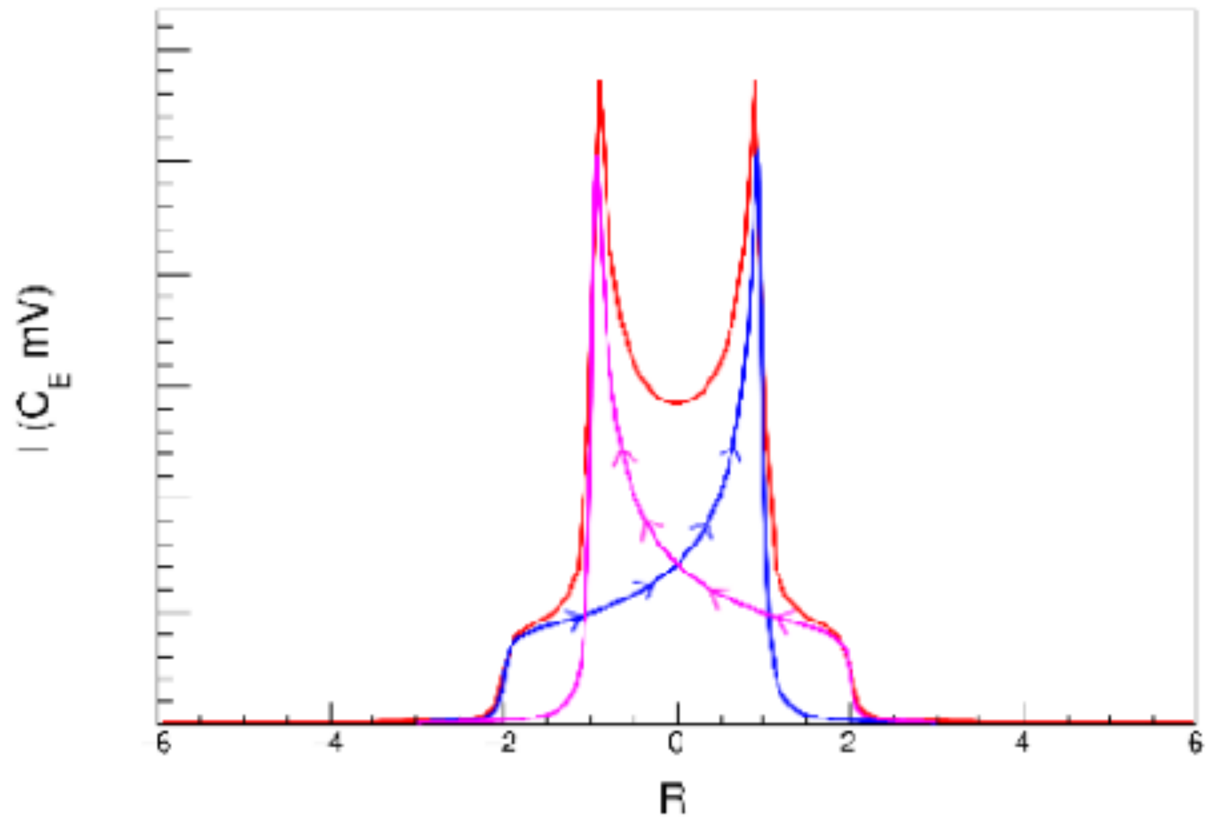
θ is orientation of the coupled spin packets along the NMR line

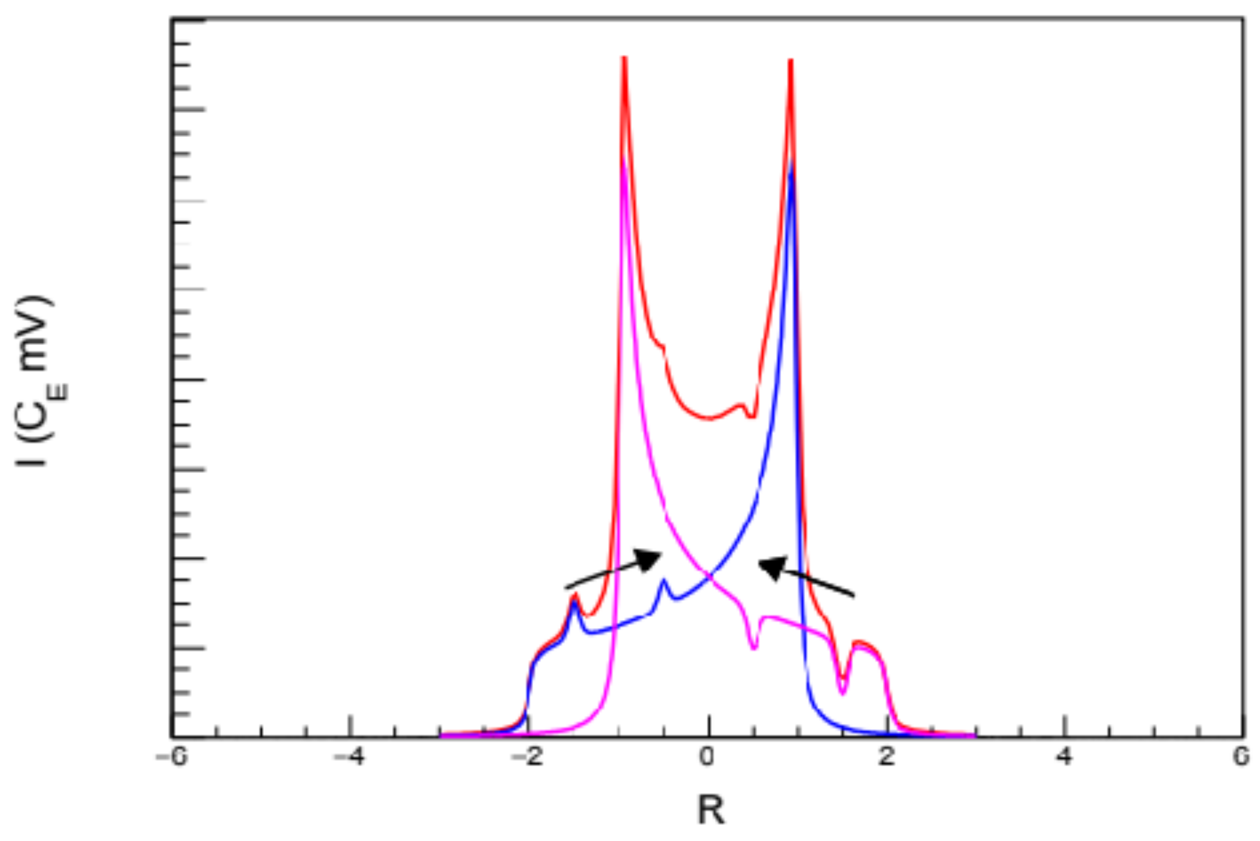
Higher Tensor Polarization Benchmark

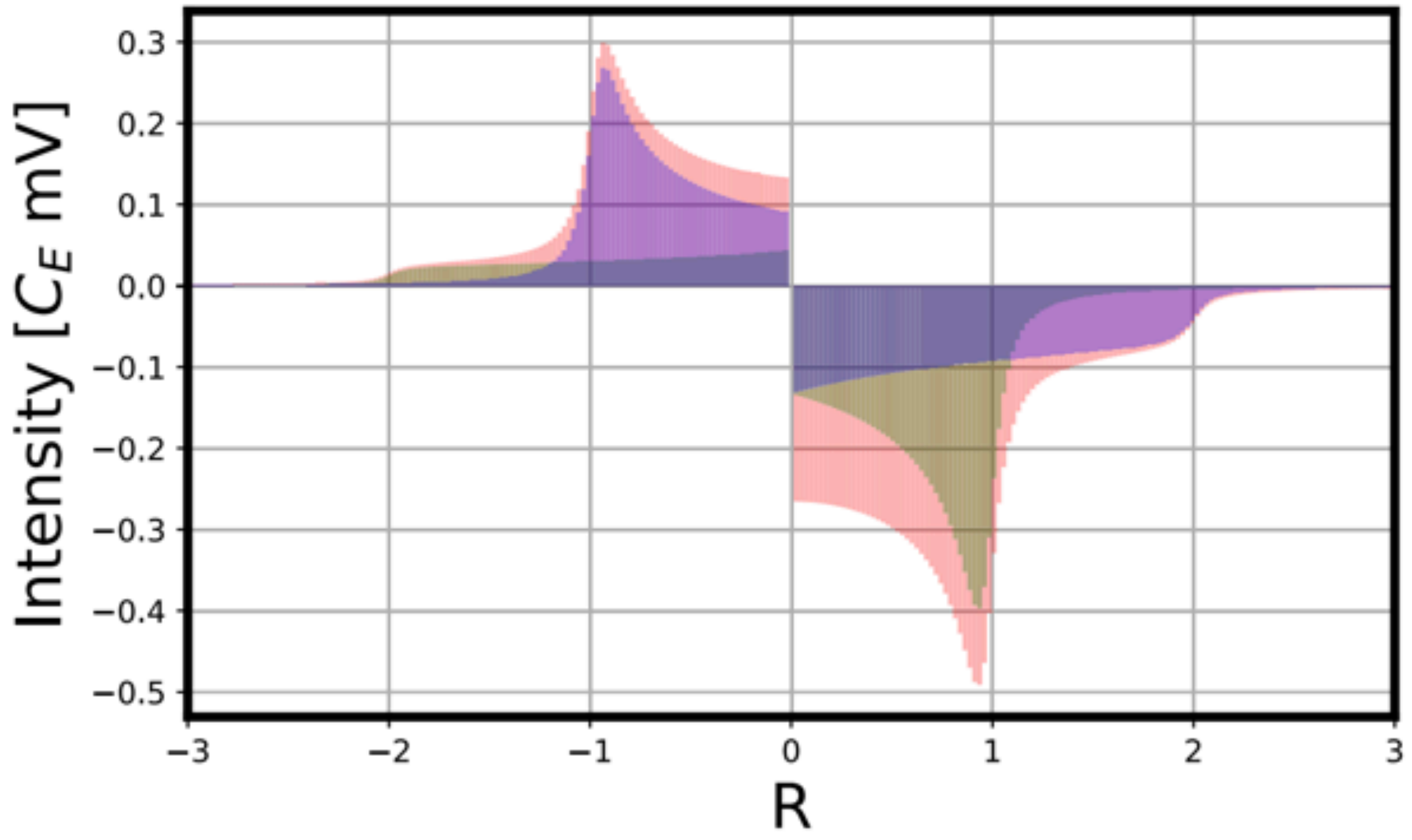
Under certain conditions

- We’ve hit the conditional 30% but were told we would not pass the ERR being it was not under experimental conditions: what should we be working towards?

- If we need higher Pzz we must be putting effort into rotation, single crystals, and second generation configurations: lower temperature, higher field and lower intensity (<30 nA). This is expensive research.







Scattering Experiments to Verify

Thermal Neutron Scattering at NIST or Oak Ridge

- Measure Vector and Tensor parts and characterize
- Enhance and do it again
- Need portal DNP system
- Rotating target
- Multiple experiments
- …and so on.

$$A_2(\theta) = \frac{T(\theta) - T(90^\circ)}{T(\theta) + T(90^\circ)} \quad \text{(tensor sensitive)}$$

$$T(\theta) \;\approx\; \exp\big[-nL\,\sigma_0\big]\;\exp\Big[-nL\,C_t\,P_{zz}\,\tfrac{1}{2}(3\cos^2\theta - 1)\Big]$$

Fit $A_2(\theta)$ to $C\,P_{zz}\,\frac{1}{2}(3\cos^2\theta - 1)$ to extract P_{zz} with minimal dependence on beam polarization P_n

Holding field is tilted by θ

Tensor Enhancement Status

ss-RF Enhanced Measurements					
Peak (MHz)	Amp (mV)	Pedestal (MHz)	Amp (mV)	P_{zz} (%)	Error (%)
32.62(0.000)	20	32.85(0.015)	70	26.7	5.4
32.63(0.015)	30	32.85(0.020)	40	28.8	5.7
32.64(0.015)	30	32.84(0.025)	40	29.4	7.2
32.64(0.015)	25	32.83(0.035)	20	26.5	6.8
32.64(0.015)	20	32.85(0.035)	70	30.3	7.8
32.64(0.020)	20	32.85(0.025)	40	27.5	4.7
32.64(0.015)	40	32.88(0.055)	50	31.1	8.5

Basic ss-RF

rss-RF Enhanced Measurements						
Ω^{-1}	Peak (MHz)	Amp (mV)	Pedestal (MHz)	Amp (mV)	P_{zz} (%)	Error (%)
50	32.65(0.010)	15	32.85(0.015)	45	35.7	8.4
44	32.66(0.000)	10	32.88(0.015)	40	36.5	9.7
40	32.65(0.000)	15	32.88(0.015)	40	36.3	9.3

Rotating ss-RF

Plans

But does it help us for the ERR

- Do we need to have and test cold irradiate ND3?
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- Do we need to fully characterize spin diffusion (with and without DNP)?
- Do we need a to reach a higher benchmark for tensor polarization under certain conditions?
- Do we need to prove with scattering data that modern lineshape theory is correct?
- Should we instead focus on run configuration and overall FOM?
- *ss-RF hardware (easy setup vs optimal setup)*
- *AFP (and coil configuration) optimized for our field orientation*

Summary

- We understand ND3 and the lineshape theory better than ever before.
- We understand how to Tensor Enhance better than every before.
- We understand how to configure run cycles for these types of experiments better than ever before.
- What's next?