Analysis of the Complex NMR Lineshape of the Deuteron

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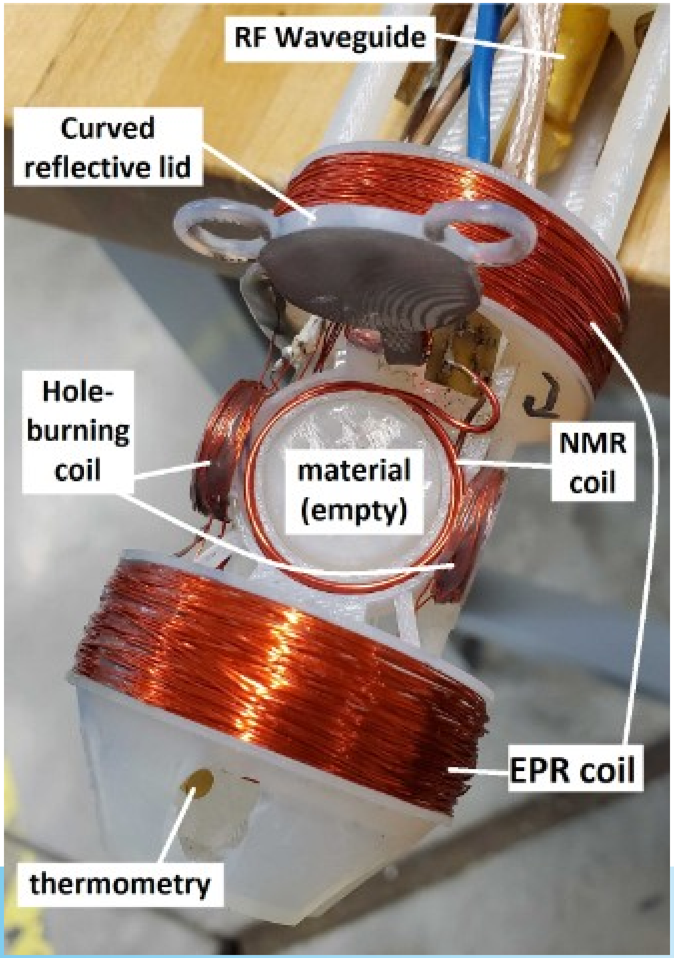
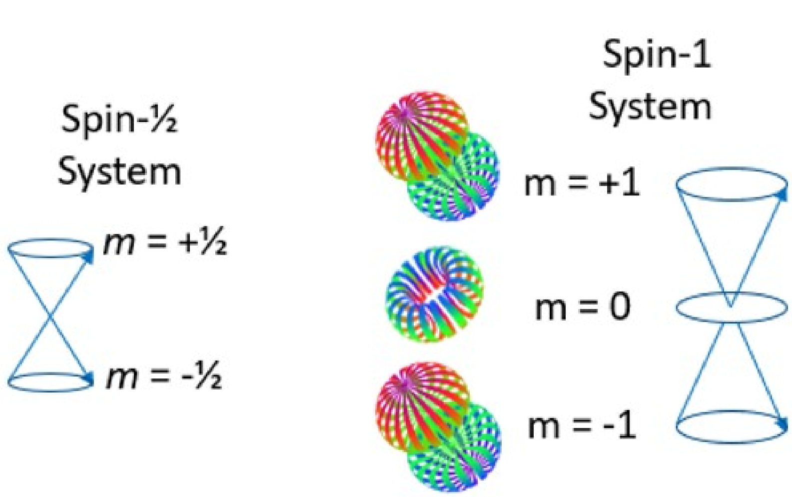
Outline

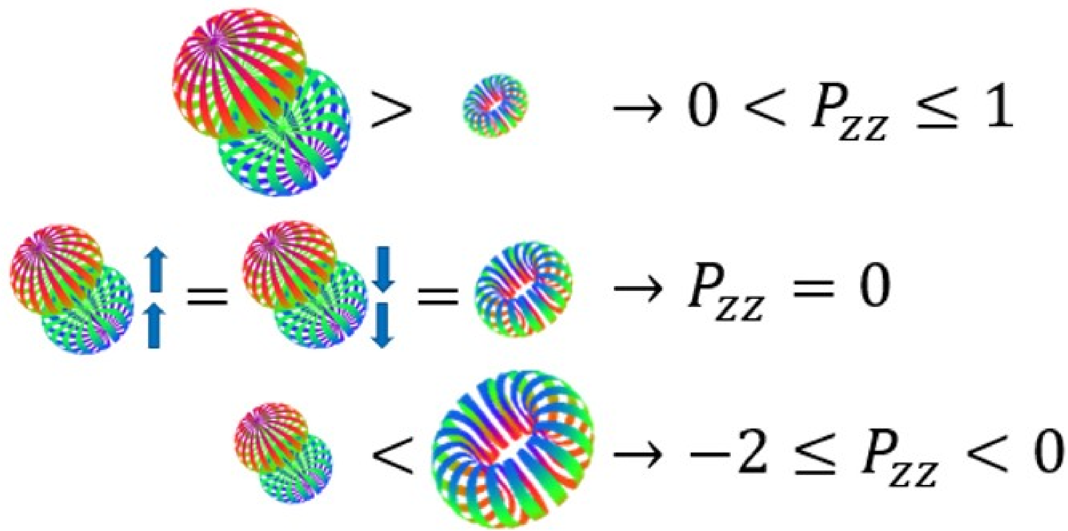
- Background
- Functional form for deuteron NMR lineshape
- Complex NMR signals
- Scaling complications
- Enhancement techniques
- Future plans



Background

- Solid Polarized Target Group at UNH
  - developing dynamically polarized target
  - measure spin-structure & tensor spin observables
    - A_{ZZ}, T_{20} and b_1

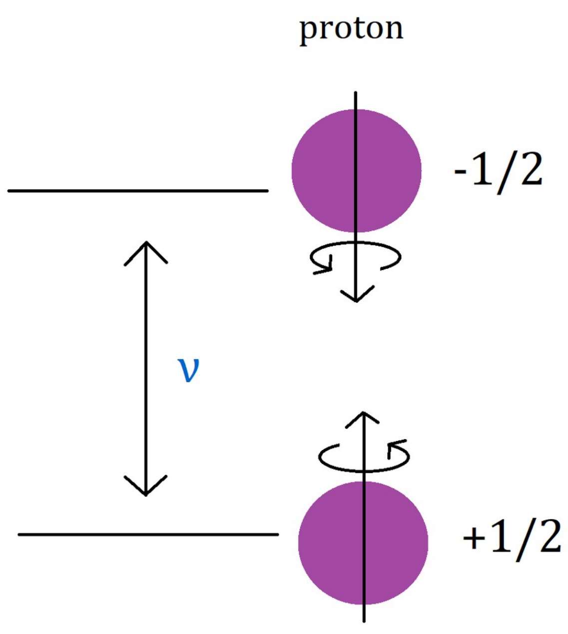


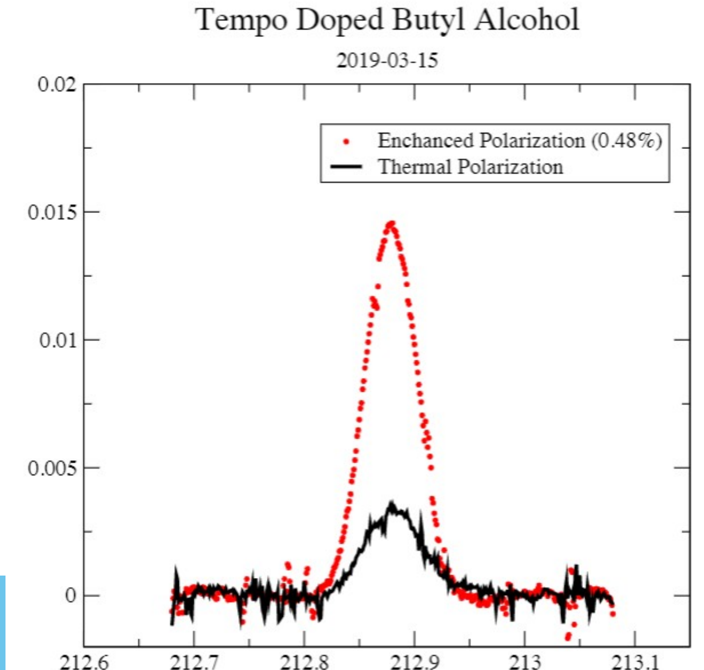


E. Long et al., C-12-15-005 PAC 44 (2016)

Proton Signals

- Spin polarized protons: low T, high B → energy gap between spin states → uneven distribution
  - Thermal equilibrium (TE) signal – can be enhanced
  - Detectable through nuclear magnetic resonance (NMR)
  - Area under curve → % vector polarization (P)

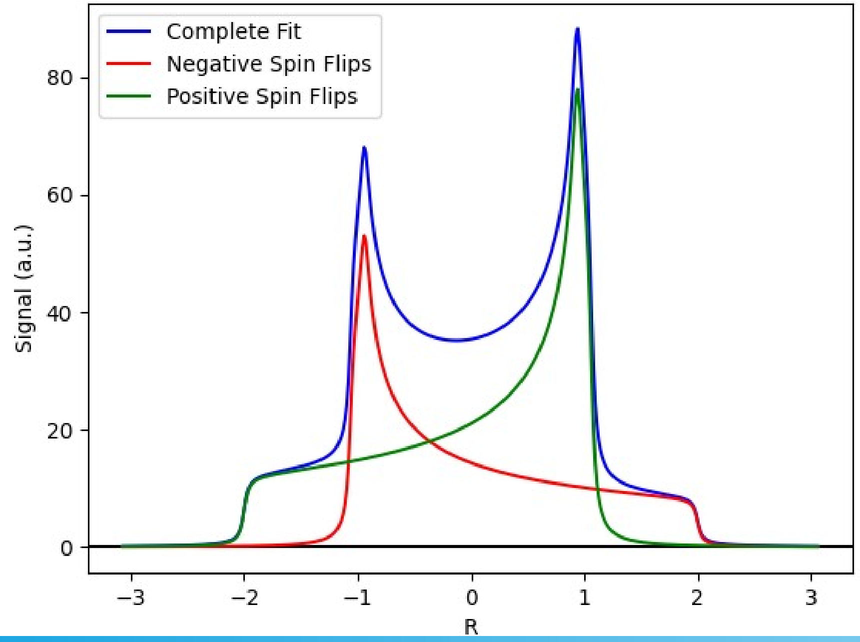


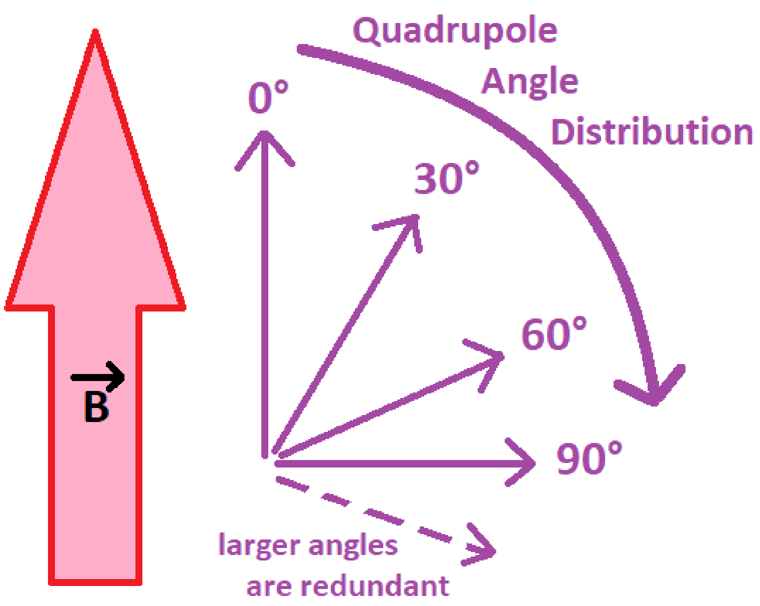


One of our first signals!

Deuteron Signals

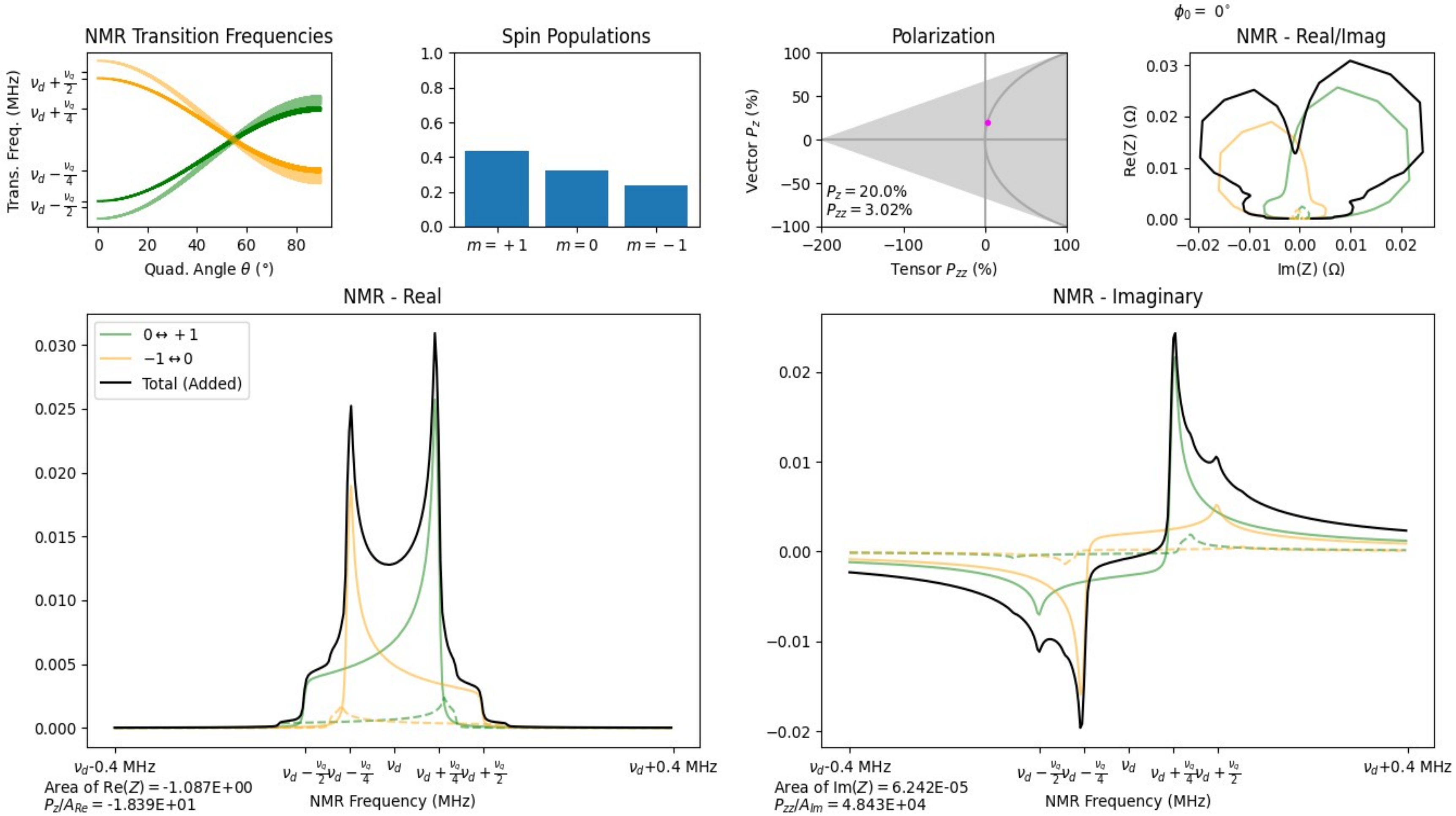
- Deuteron signal (with quadrupole splitting) more complex:
  - One curve for -1 → 0, another for 0 → +1 – sum gives P, difference gives Q
  - Curves span quadrupole angle distrubtion, 0-90° (up to 180° doubles back)
- Ideally, NMR signal would be compared to TE signal and scaled
  - TE integral is physical quantity dictated by B, T
  - At 5T & 1K: P for deuteron ~ 0.08% - on level of noise for our lab





Simulating Spin Flips

- Macro that directly simulates spin flips for a given polarization
- Can use to explore new avenues for increasing Q



Plots from code by Elena Long, drawing on: M. H. Cohen et al., Solid State Physics 5, 321 (1957)

NMR Analysis

R, A, η, ϕ → compacting variables

$$Y = \sqrt{3 - \eta\cos(2\phi)}$$

$$\rho^2 = \sqrt{A^2 + [1 - \epsilon R - \eta\cos(2\phi)]^2}$$

$$\cos(\alpha) = \frac{1 - \epsilon R - \eta\cos(2\phi)}{\rho^2}$$

$$R = \frac{\omega - \omega_d}{3\omega_q}$$

$$-3 \leq R \leq 3$$

functional form of signal

$$f_\epsilon(R, A, \eta, \phi) = \frac{1}{2\pi\rho}\{2cos(\frac{\alpha}{2})\left[arctan\left(\frac{Y^2 - \rho^2}{2Y\rho sin(\frac{\alpha}{2})}\right) + \frac{\pi}{2}\right] + sin(\frac{\alpha}{2})ln\left(\frac{Y^2 + \rho^2 + 2Y\rho cos(\frac{\alpha}{2})}{Y^2 + \rho^2 - 2Y\rho cos(\frac{\alpha}{2})}\right)\}$$

$$\epsilon = \pm 1$$

phi average

$$F_\epsilon \approx \frac{1}{J+1}\sum_{j=0}^{J}\frac{\sqrt{3}f_\epsilon(R, A, \eta, \phi_j)}{\sqrt{3 - \eta cos(2\phi_j)}}$$

positive & negative spin flips

$$\chi''(r, R) \propto \frac{1}{\omega_q}\left\{\left[\frac{r^2 - r^{1-3\theta R}}{r^{1-\theta R}}\right]F_+(R) + \left[\frac{r^{1+3\theta R} - 1}{r^{1+\theta R}}\right]F_-(R)\right\}$$

$$\theta = \omega_q/\omega_d$$

- Without reliable TE, curve fit NMR lineshape to known formula from Dulya, et al.
- At high P, physical parameters can be extracted – B, T not required!
- With parameters, curve fit for *r* across timespan for data taking
  - Naively, ratio of peak heights of signal
  - Instead of area method, *r* is used for ratio method to find both P and Q

$$\mathcal{P} = \frac{r^2 - 1}{r^2 + r + 1} \quad \text{or} \quad \mathcal{Q} = \frac{r^2 - 2r + 1}{r^2 + r + 1}$$

- In materials with different bonds to deuterium (e.g. butanol – C and O bonds), set of curves for each bond type

C. Dulya et al., Nuclear Instruments and Methods in Physics Research A 398 (1997)

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positive & negative spin flips ⇩

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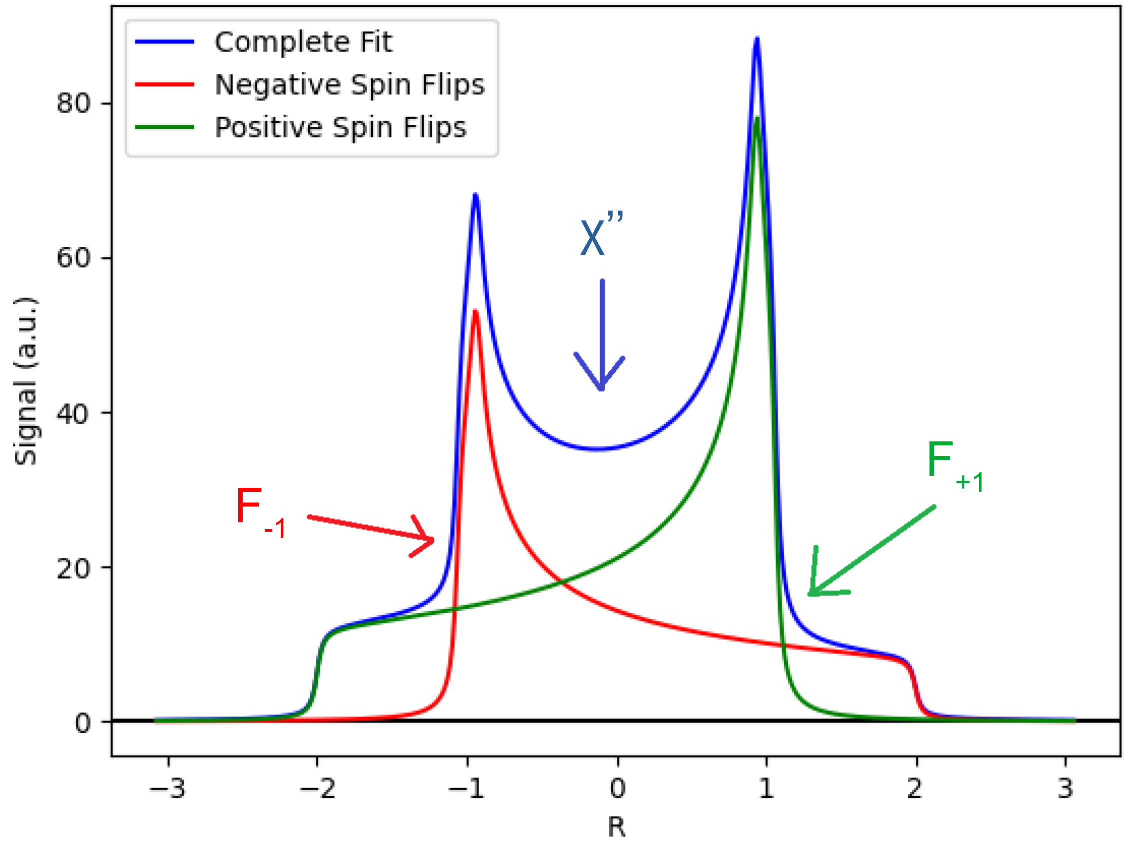
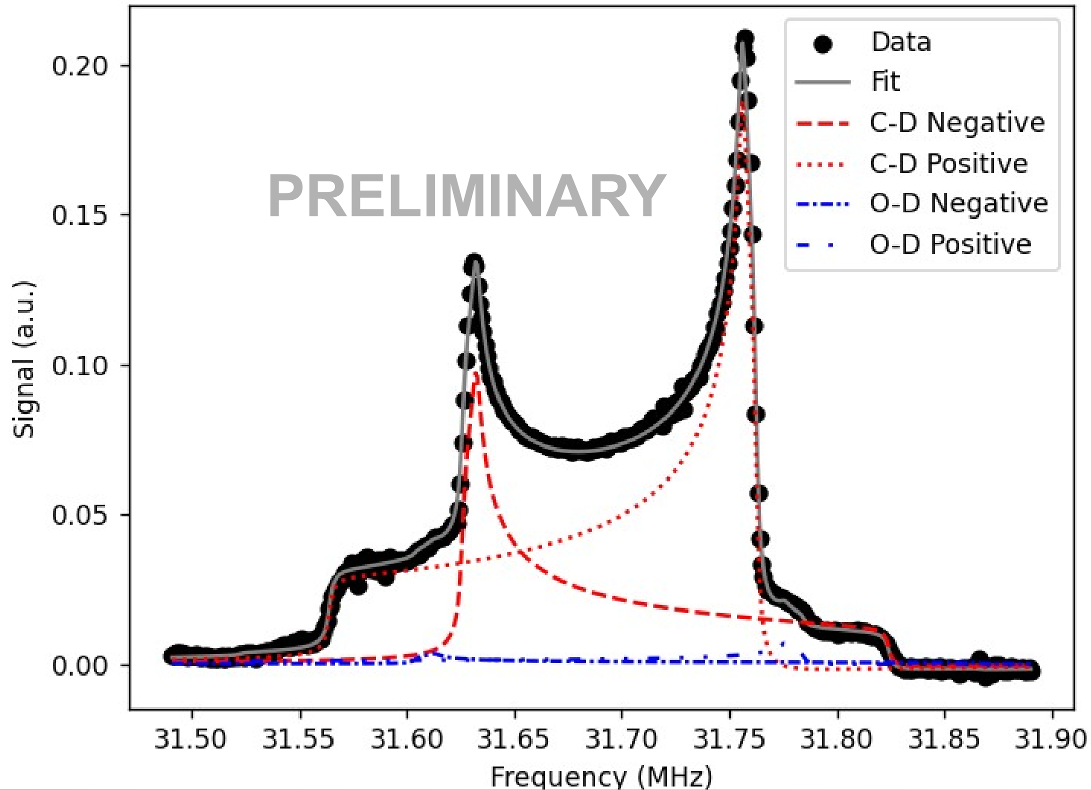


C. Dulya et al., Nuclear Instruments and Methods in Physics Research A 398 (1997)

Data Analysis

- Passing deuteron signal data through curve fitting routine based on Dulya yields good fit
  - Component spin-flip curves can be reconstructed from curve fitting parameters
  - Can perform both area and ratio methods!
- Passing simulated data through routine extracts P that agrees with input!



- P = 43.0%
- Q = 14.4%

Real & Imaginary Analysis

- Issue with Dulya – “false asymmetry” – seems artificial – why not just fit both real and imaginary parts of signal?
- Two different parts to signal – absorptive and dispersive – rotate between through phase angle
  - Real = χ’’ cosθ - χ’ sinθ
  - Imag. = χ’’ sinθ + χ’ cosθ
- Changes for dispersive:

functional form of signal ⇩

$$f_\epsilon(R,A,\eta,\phi) = \frac{1}{2\pi\rho}\{2\sin(\frac{\alpha}{2})\left[arctan\left(\frac{Y^2-\rho^2}{2Y\rho sin(\frac{\alpha}{2})}\right)+\frac{\pi}{2}\right] + \cos(\frac{\alpha}{2})ln\left(\frac{Y^2+\rho^2+2Y\rho cos(\frac{\alpha}{2})}{Y^2+\rho^2-2Y\rho cos(\frac{\alpha}{2})}\right)\}$$

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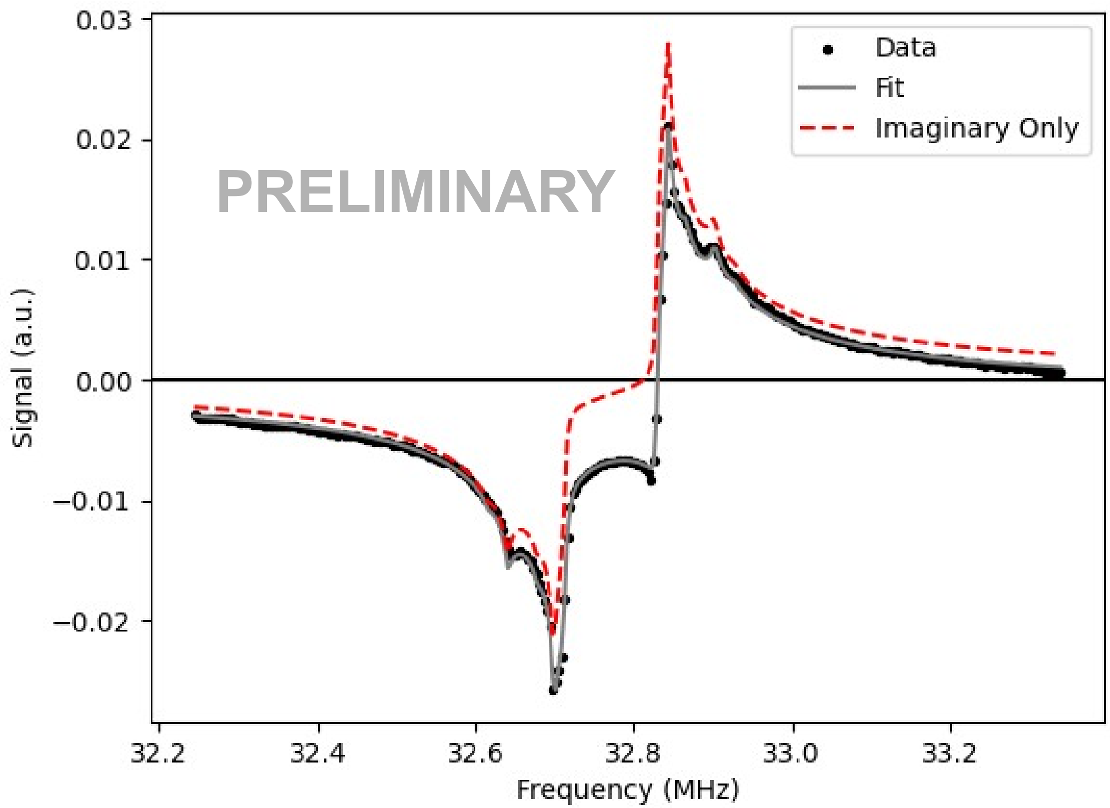
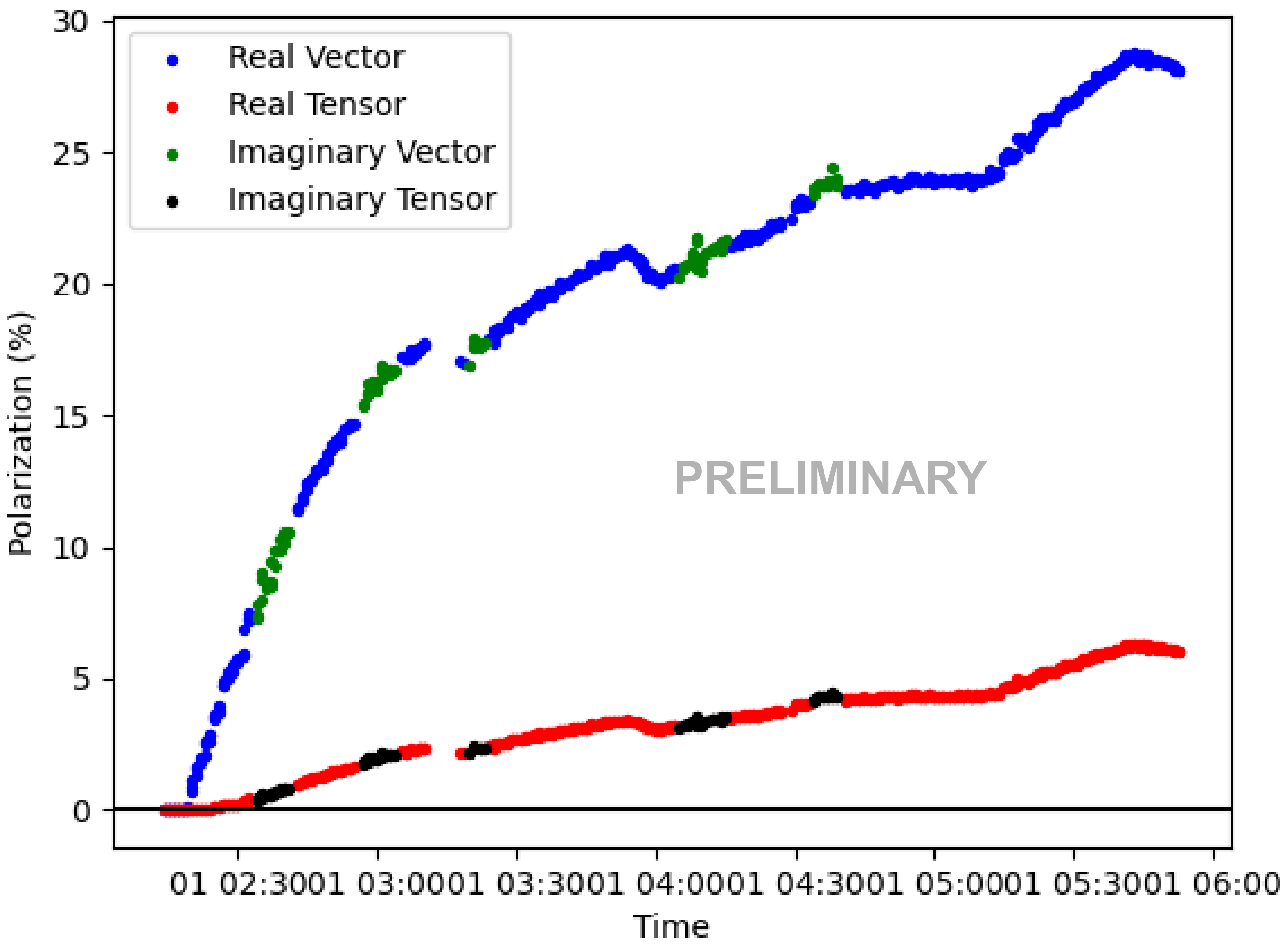


Real & Imaginary Analysis

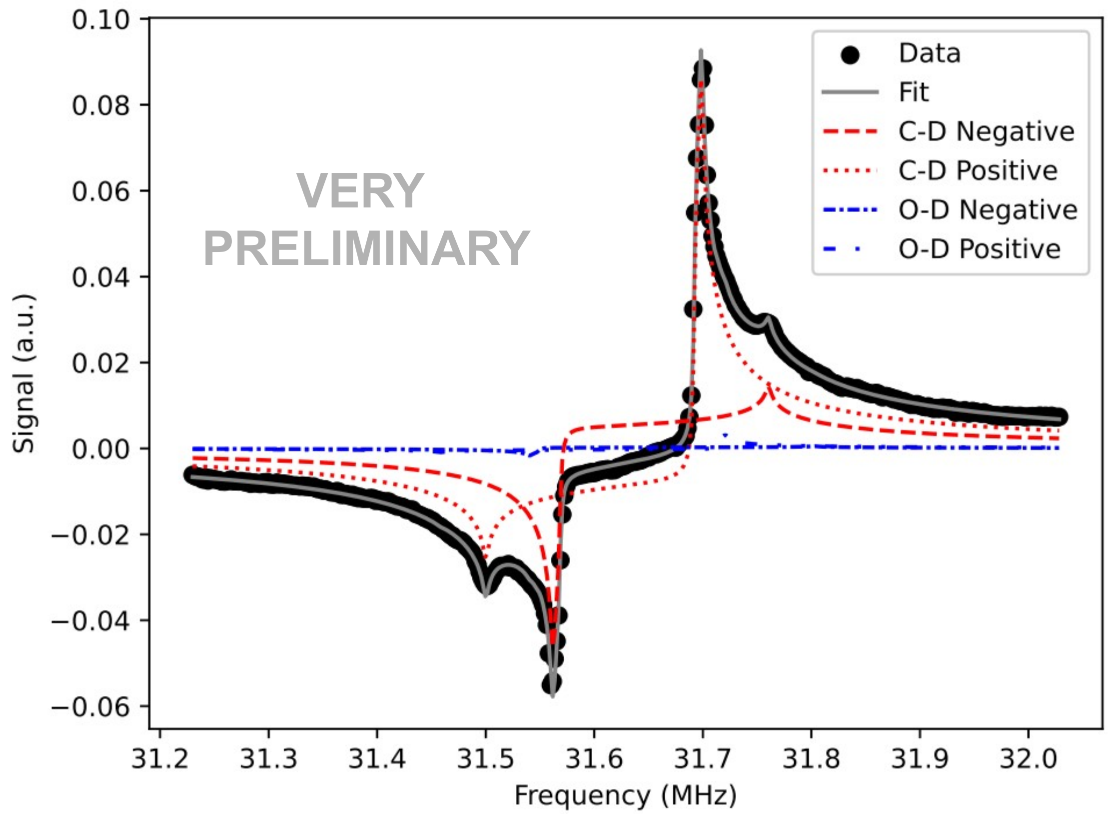
- Preliminary agreement between P and Q taken from real and imaginary signals!

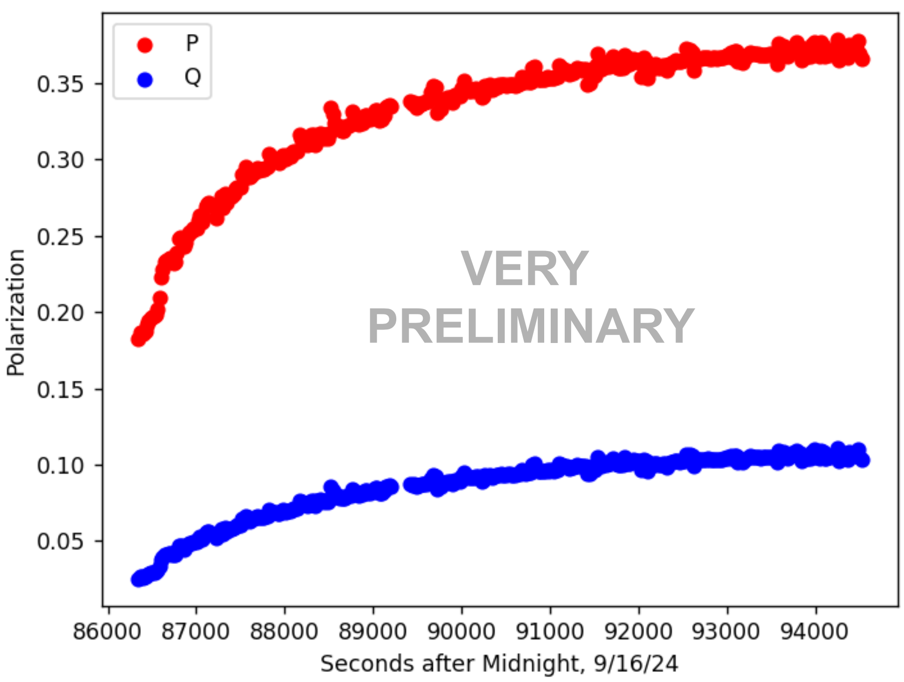


Fully Imaginary Analysis

Ran full spin-up curve entirely in the imaginary (88.5° phase!)

- Peaked at P = 37%, Q = 10.5%

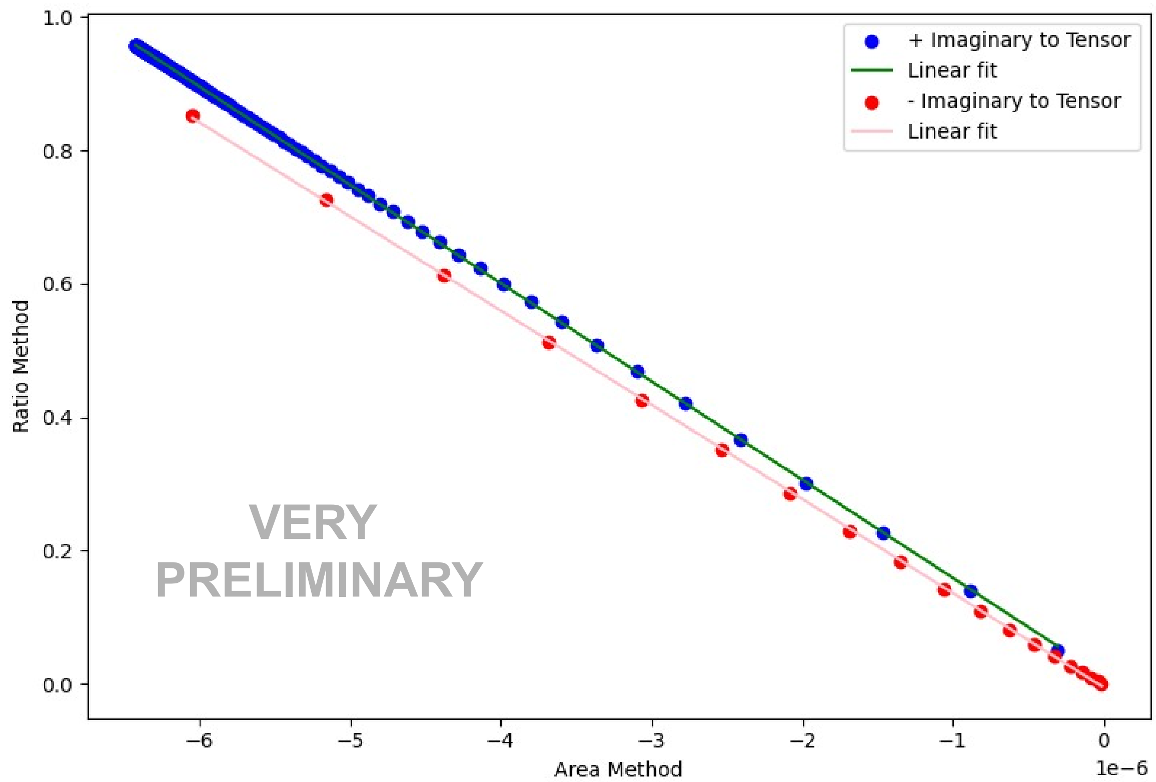




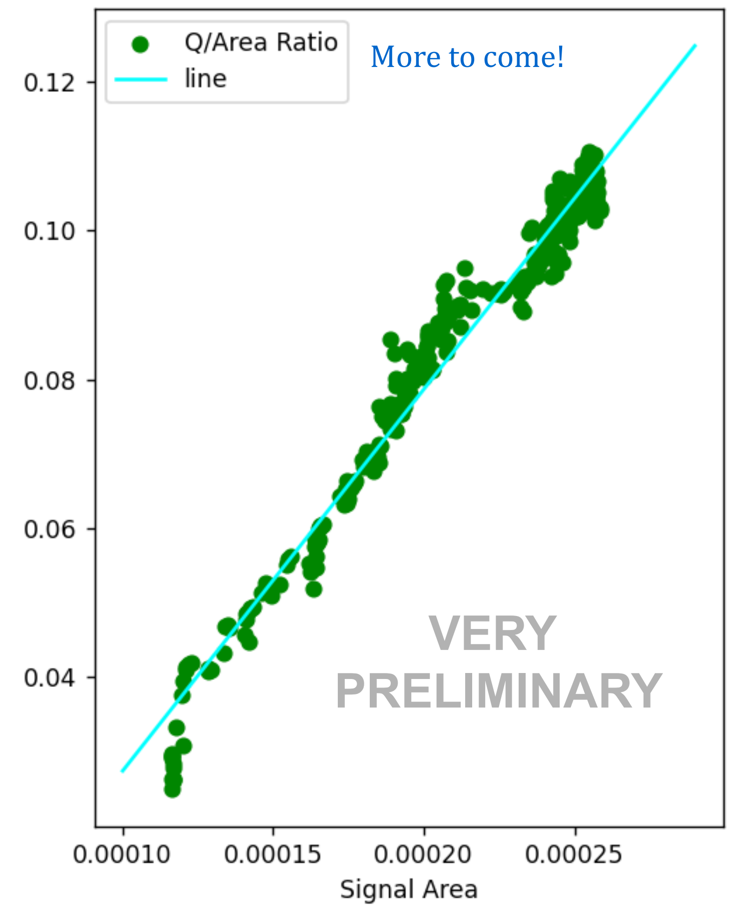
Why Imaginary?

Complex is more accurate – tuning is difficult!

Real area ∝ P, simulations suggest Imaginary area ∝ Q



Very first purely imaginary spin-up!

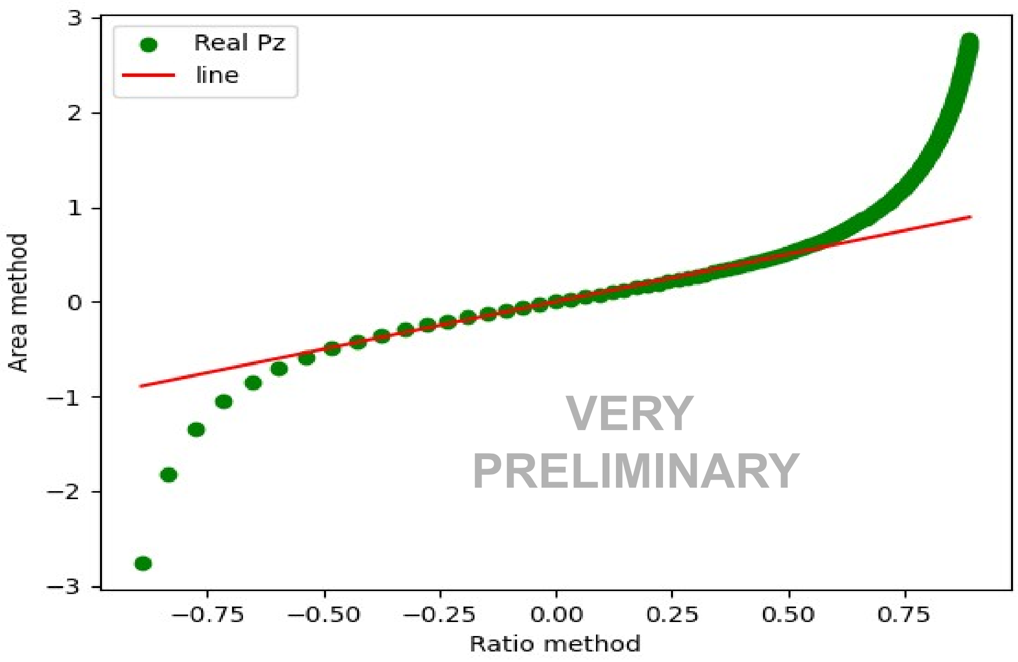


Keeping Accuracy at High P

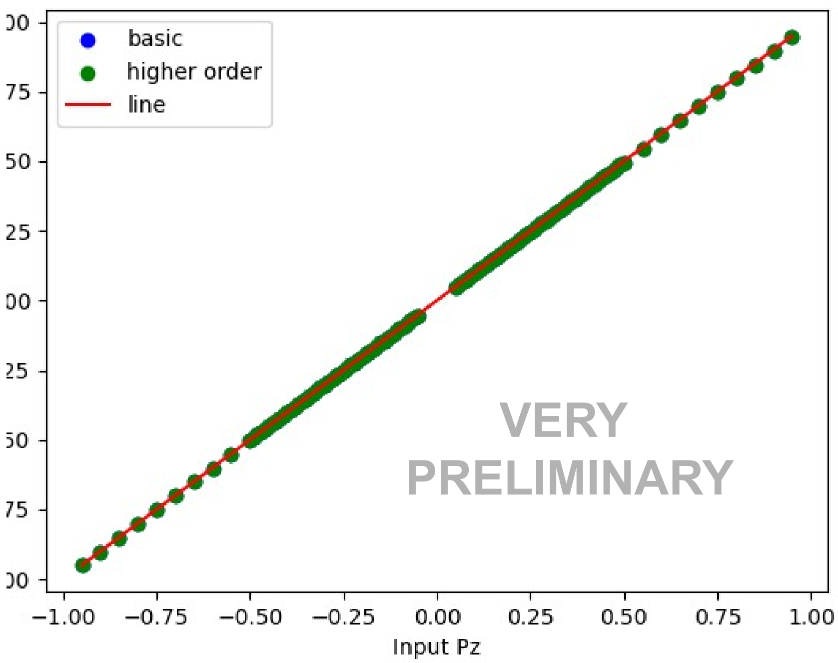
Dulya function is missing a final outer parameter: Ξ, which varies with P, more noticeably at high P

Seems to be quartic-ly dependent on r – more analysis needed

Ξ assumed constant:

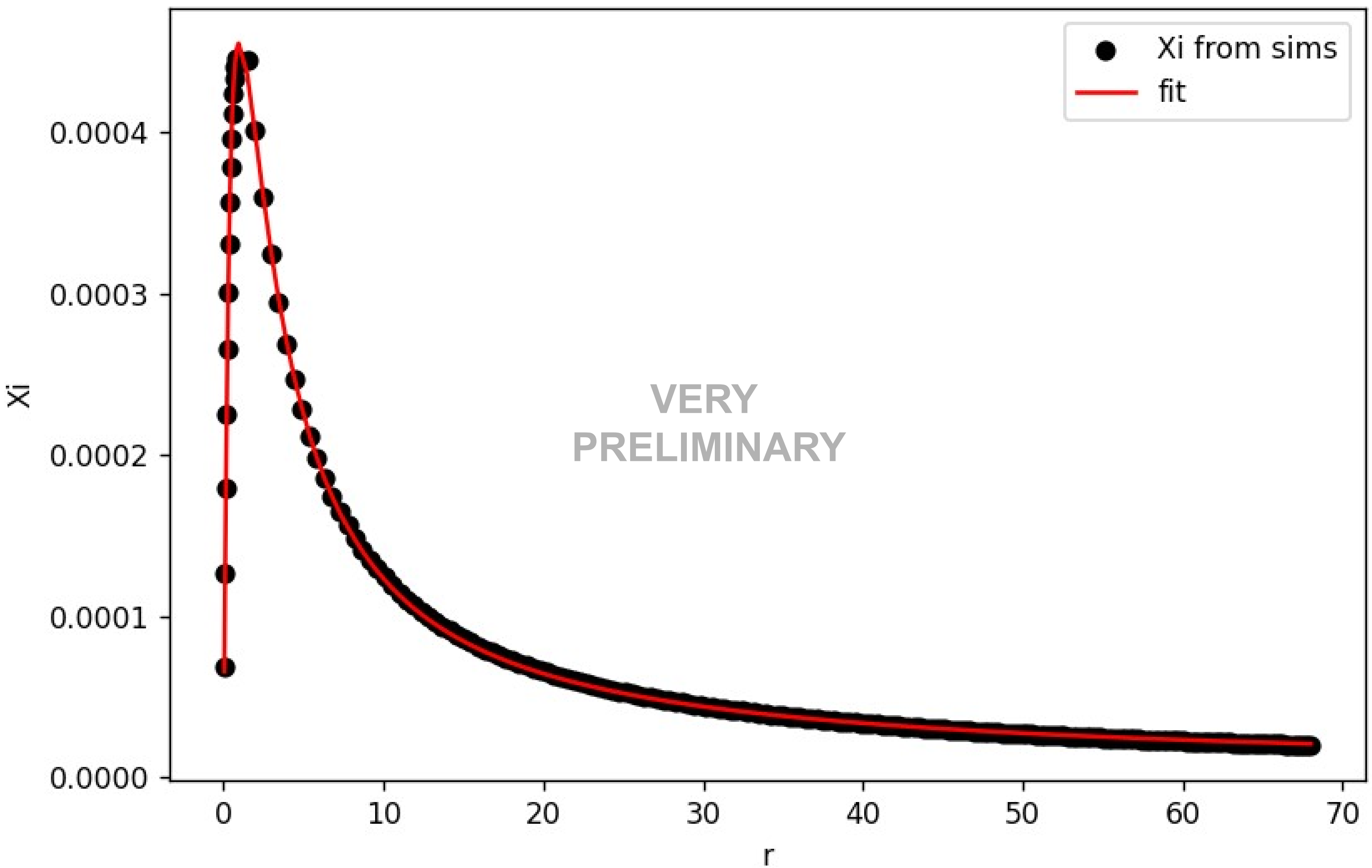


Ξ allowed to float:



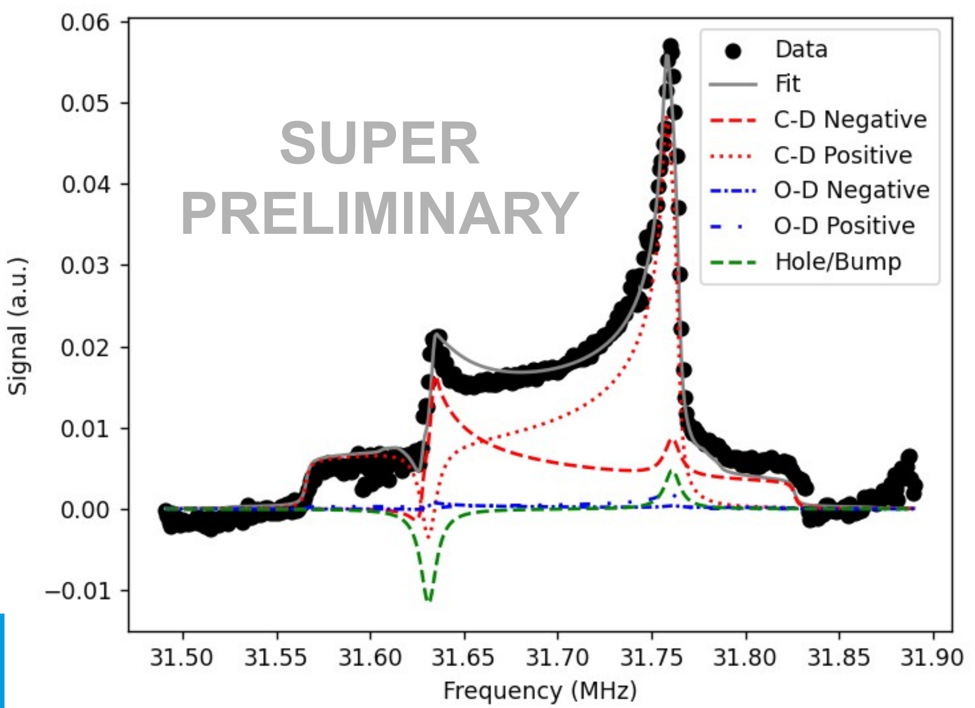
Quartic Relationship: Ξ v P

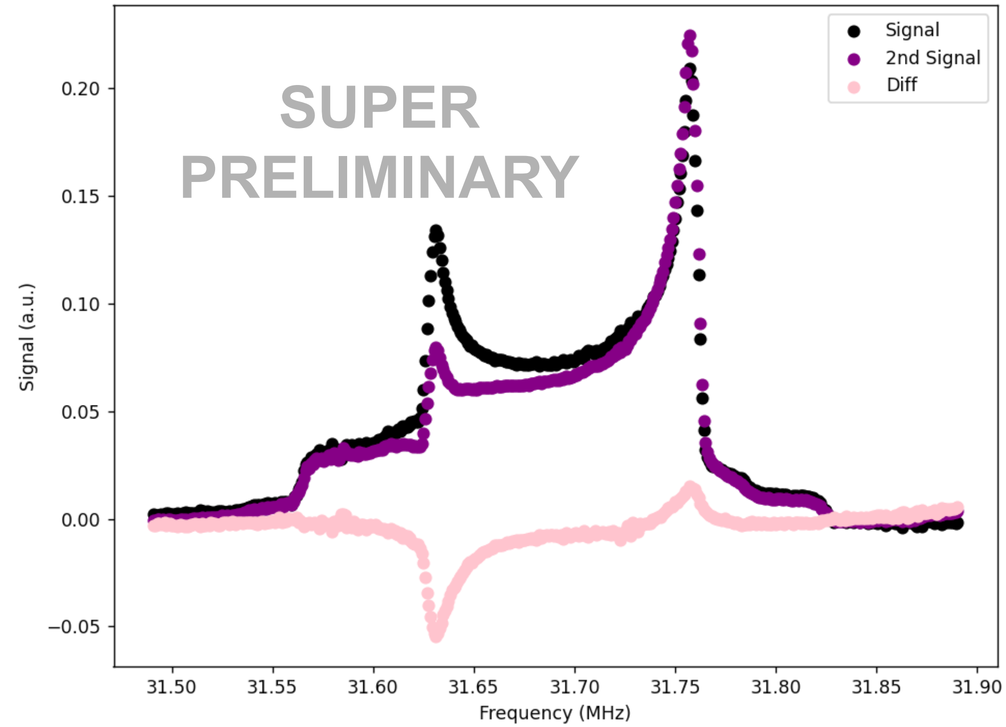
$\Xi \propto -0.38\, P^4 - 0.61\, P^2 + 1$



Increasing Q

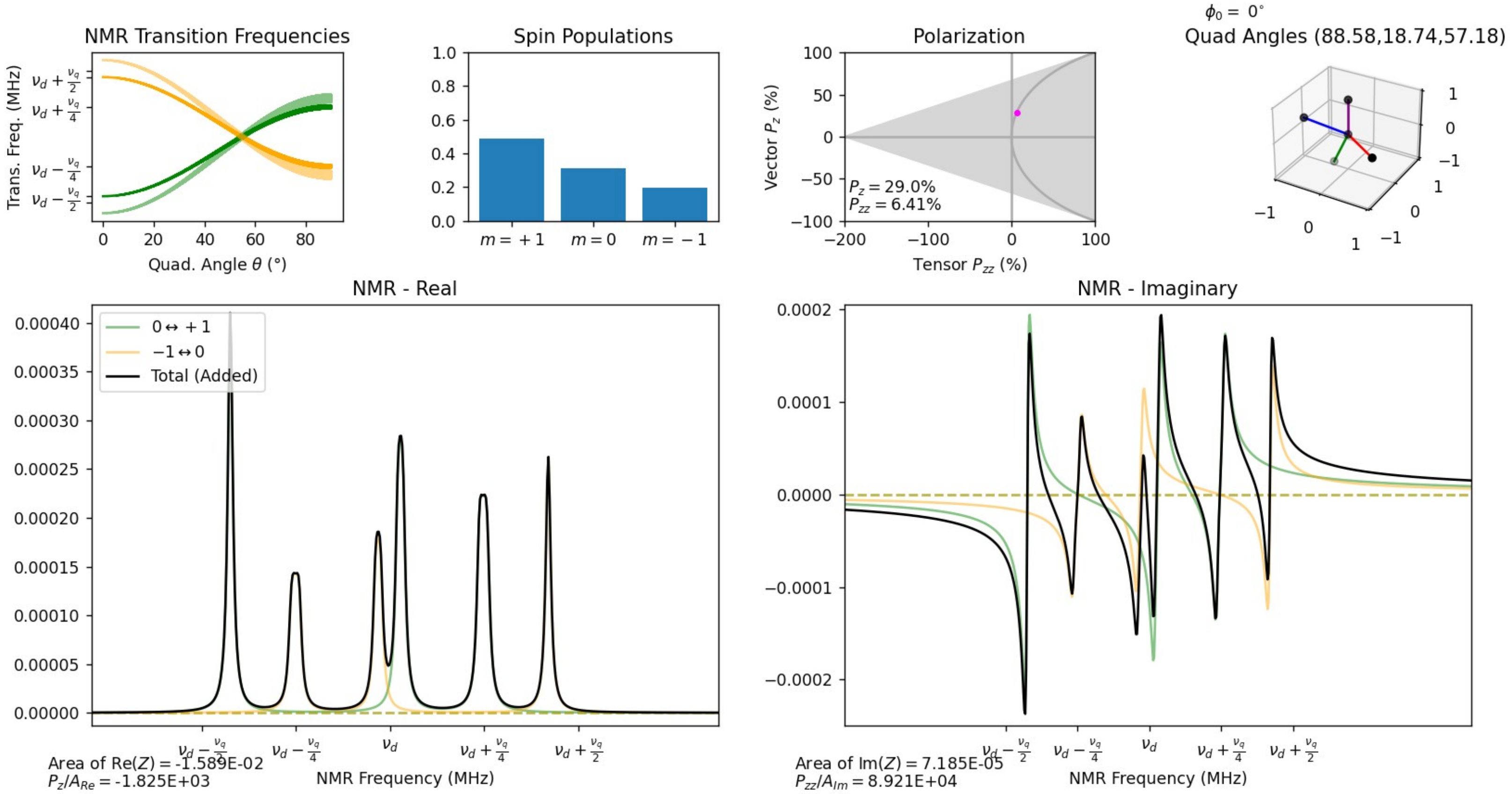
- Increasing P via mm-wave enhancement naturally gives Q
- To increase further, can use hole-burning: separate solenoid fires at specific frequency to drive spin flips – increase area difference
  - Lose some P but for A_{ZZ}, Q is more important
- System built & signal found by Nathaly Santiesteban/David Ruth!





Increasing Q

- Solid ND_3 crystal – instead of sine distribution of quadrupole angles (powder pattern), only 3 possible angles
- SUPER preliminary – simulations only, no tests so far

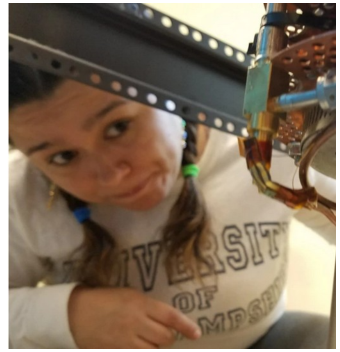


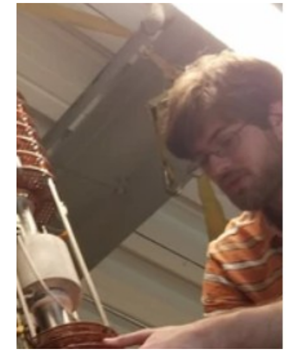
Future Goals

- Reach Q of ~30% in deuterated ammonia
  - Continue with hole-burning
  - Use EPR to focus mm-wave frequencies
- Add hole-burning to curve-fitting method – in progress!
- Confirm relationship between Q and Imaginary area
- Refine functional form of Ξ, find physical cause for it

Acknowledgments

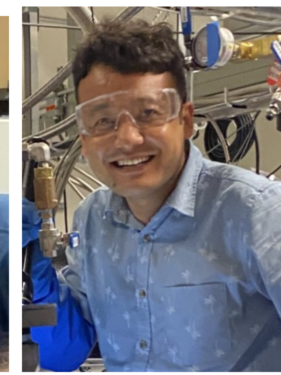
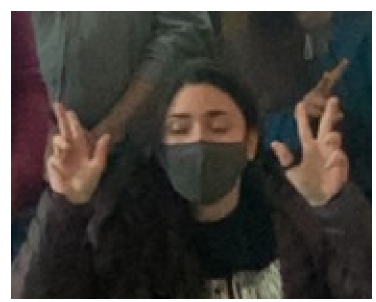
- UNH DNP PIs:
  - Elena Long
  - Nathaly Santiesteban
  - Karl Slifer




- UNH DNP collaborators:
  - Anchit Arora
  - Hector Chinchay
  - Muhammad Farooq
  - Chhetra Lama
  - Olaiya Olokunboyo
  - Eli Phippard
  - David Ruth
  - Zoe Wolters
  - Allison Zec



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Deuteron-Electron Energy Levels