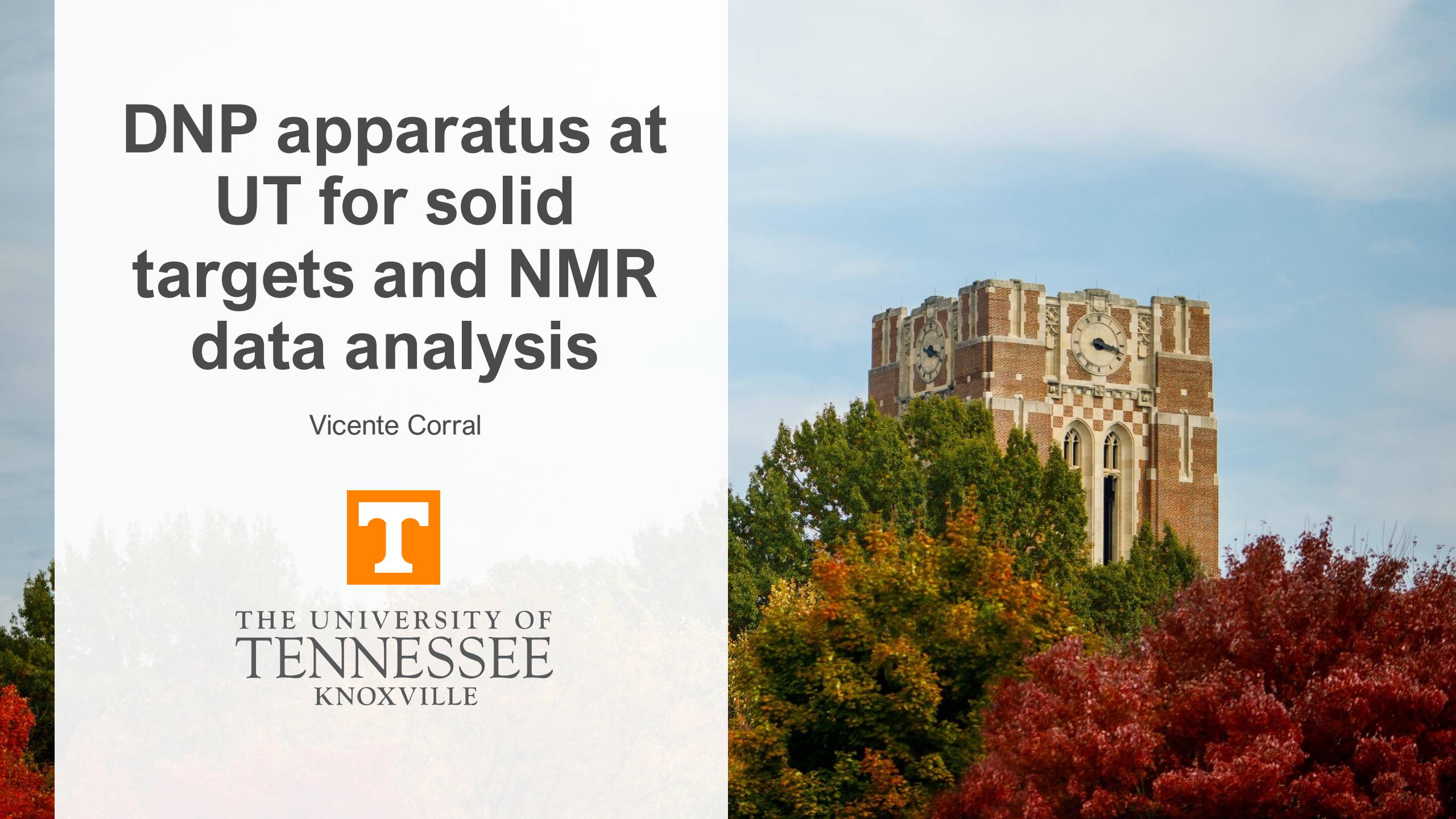
DNP apparatus at UT for solid targets and NMR data analysis

Vicente Corral



THE UNIVERSITY OF TENNESSEE KNOXVILLE

Contents

DNP system at UT

Modify ORNL DNP apparatus provided by Josh Pierce for operation at UT:

1. New insert design (Taylor M.E. undergrad)
2. Attempt to reach lower operation temperatures (collaborative effort)

- Demonstrate and maximize polarization in a variety of nuclei and proteins
- Detailed measurements of nuclear spin-relaxation times at ultra-low temperatures
- Demonstration and characterization of negative tensor polarization using AFP

C. Keith's ideas

Current Status: Dilution fridge cool down to 31.8 milli-Kelvin!

- The goal is to reach 10mK
- What may have stopped us from achieving a lower temperature:
  - Compressor has low helium pressure.
  - Did not have liquid nitrogen for nitrogen trap.
  - Openings of heat shields were not closed.

Next steps

- Attempt lower temperature cool down after resolving technical issues; test cooling power
- Assemble magnet and target volume
- Build and implement target insert once designed

Boltzmann distribution

Total number of spins

$$N_{+1} + N_0 + N_{-1} = 1$$

Vector polarization

$$P = \frac{\langle I_z \rangle}{I} = N_{+1} - N_{-1}$$

Tensor polarization (alignment)

$$Q = \frac{\langle 3I_z^2 - I^2 \rangle}{I^2} = (N_{+1} - N_0) - (N_0 - N_{-1}) = 1 - 3N_0$$

$$N_{+1} = \frac{1}{3} + \frac{P}{2} + \frac{Q}{6}$$

$$N_{-1} = \frac{1}{3} - \frac{P}{2} + \frac{Q}{6}$$

$$N_0 = \frac{1}{3}(1 - Q)$$

If the three levels are populated according to a Maxwell-Boltzmann distribution
(aka "Spin Temperature")

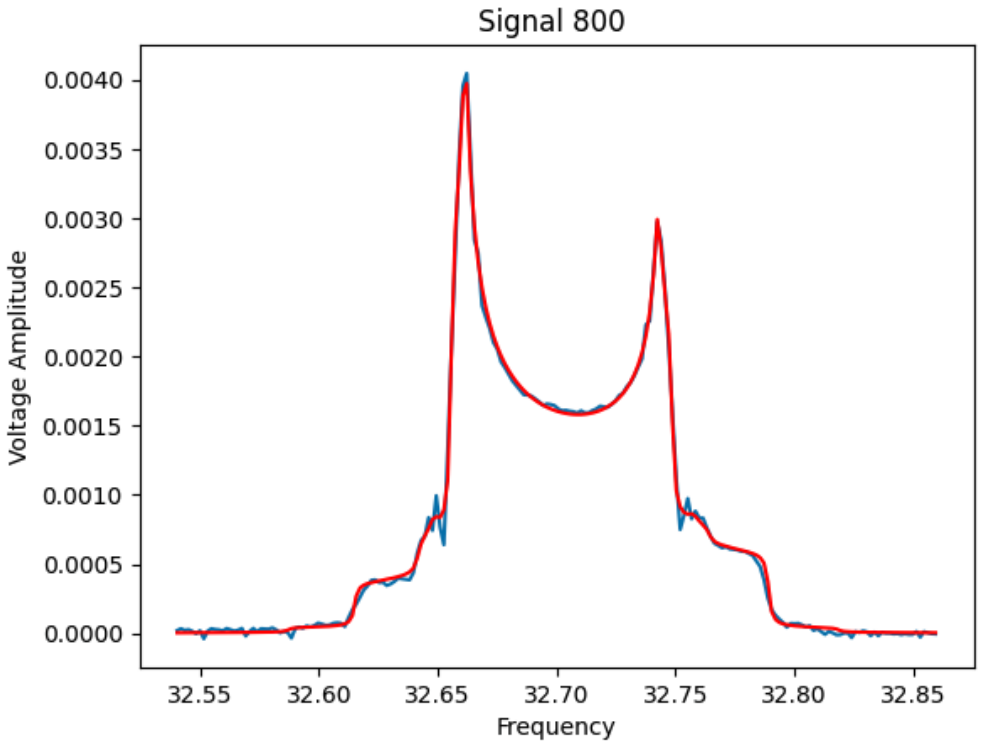
$$Q = 2 - \sqrt{4 - 3P^2}$$

$$+1 \geq Q \geq 0$$

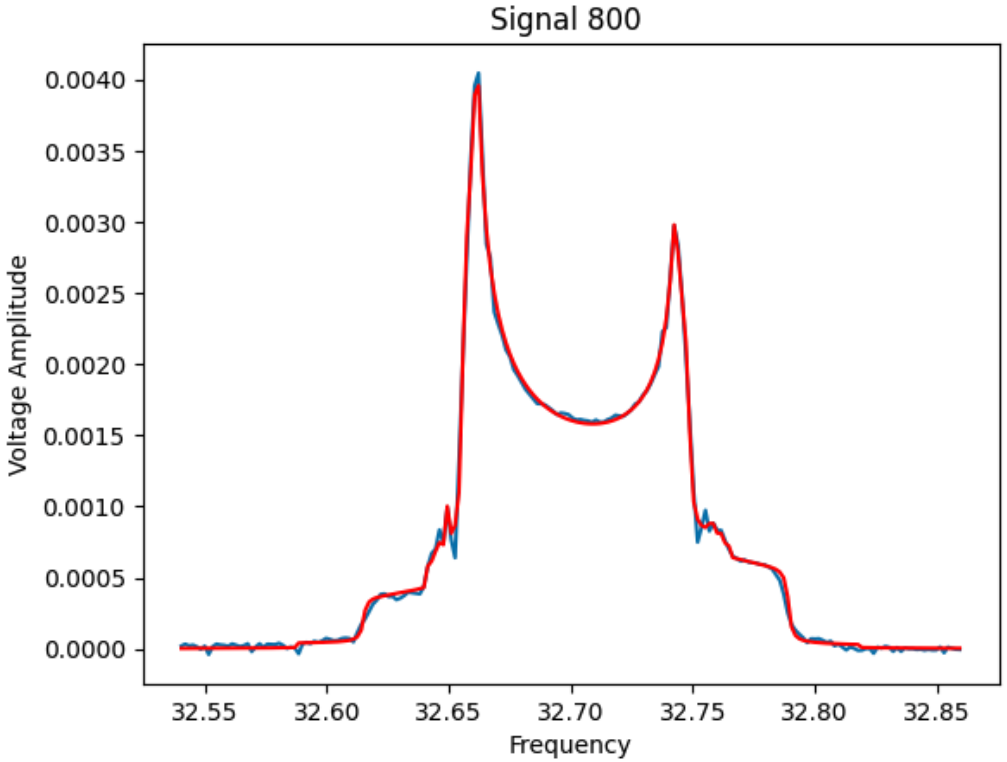
$$P = c_{cal} * Area \text{ vs } P = \frac{r^2 - 1}{r^2 + r + 1}$$

Deuterated propanediol (C3D8O2)
data from C. Keith and J. Pierce
during FROST experiment

r parameter for each bond, low polarization



Polarization: **-30.84%**

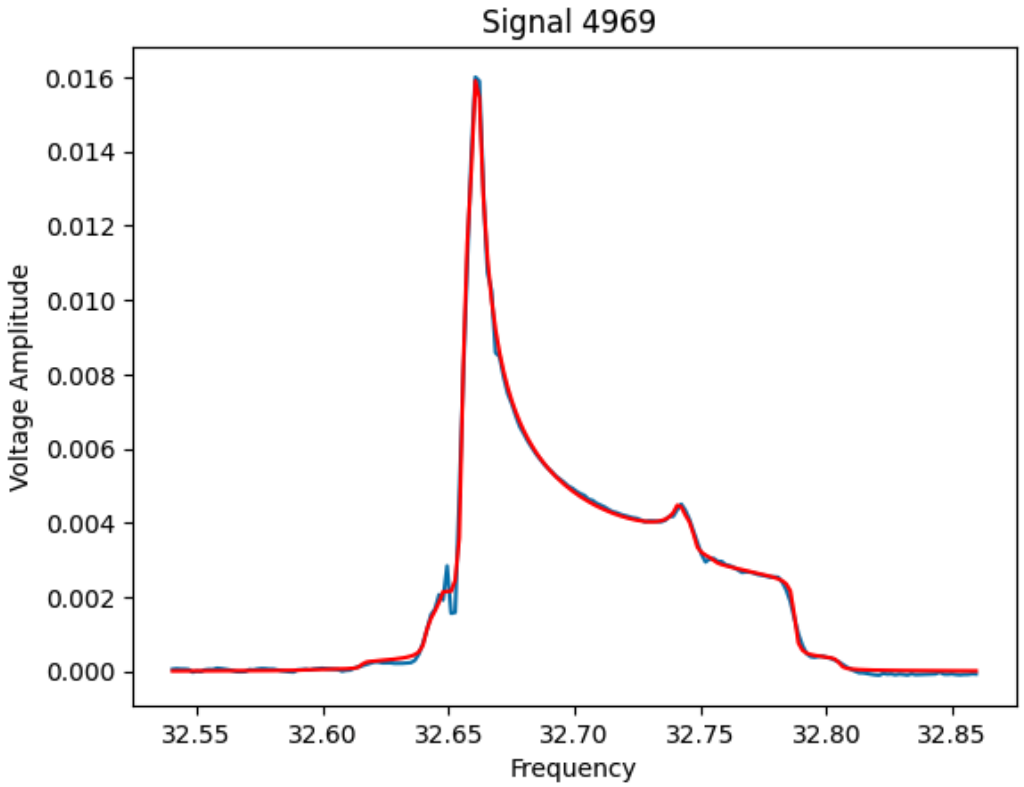


Polarization from OD: **-16.76%**

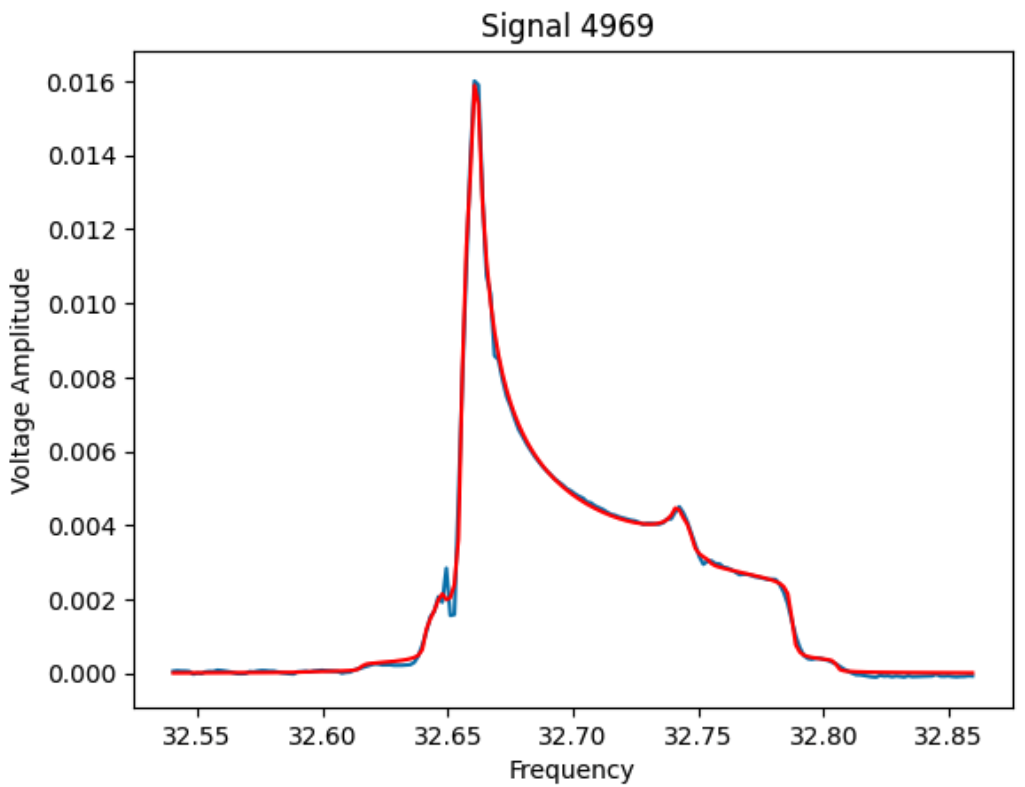
Polarization from CD: **-30.94%**

Code for fits from J. Maxwell:
https://github.com/jdmax/NMR_Analysis/tree/master

r parameter for each bond, high polarization

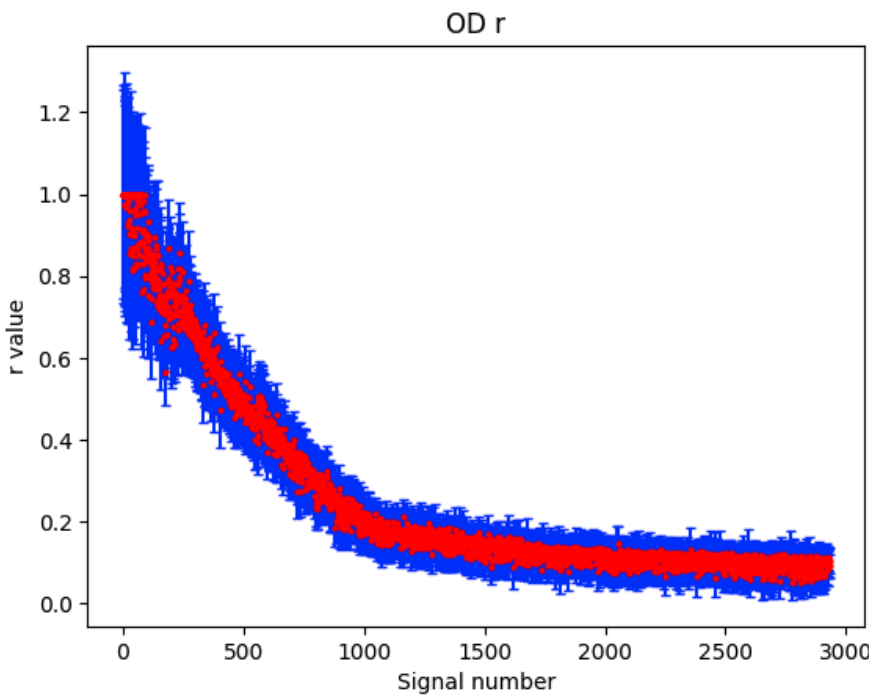


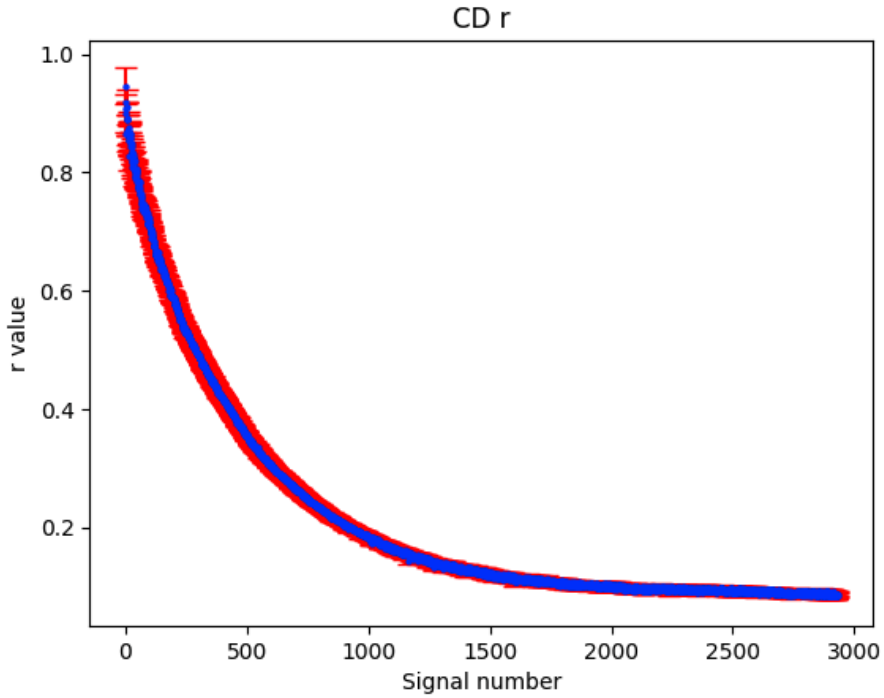
Polarization: **-90.78%**

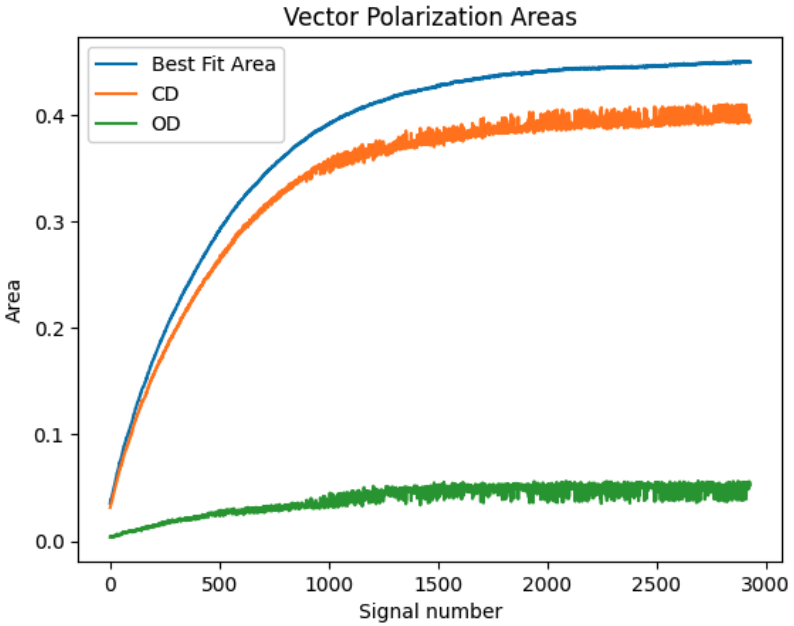


Polarization from OD: **-89.76%**
Polarization from CD: **-90.87%**

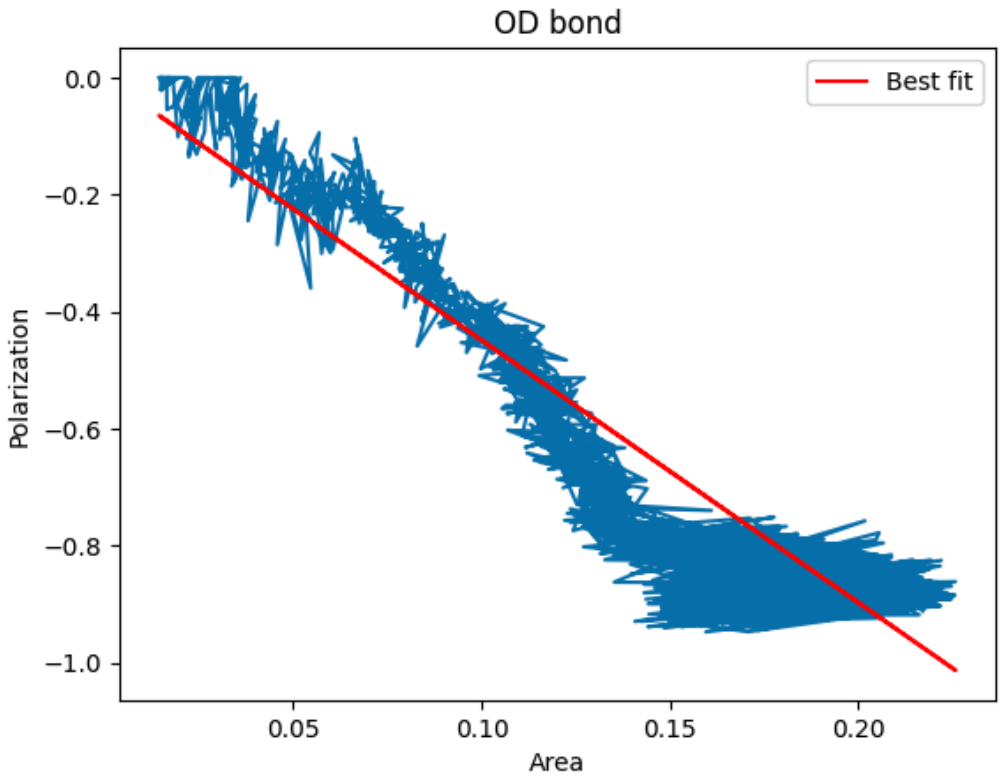
Track polarization (r) and area over time



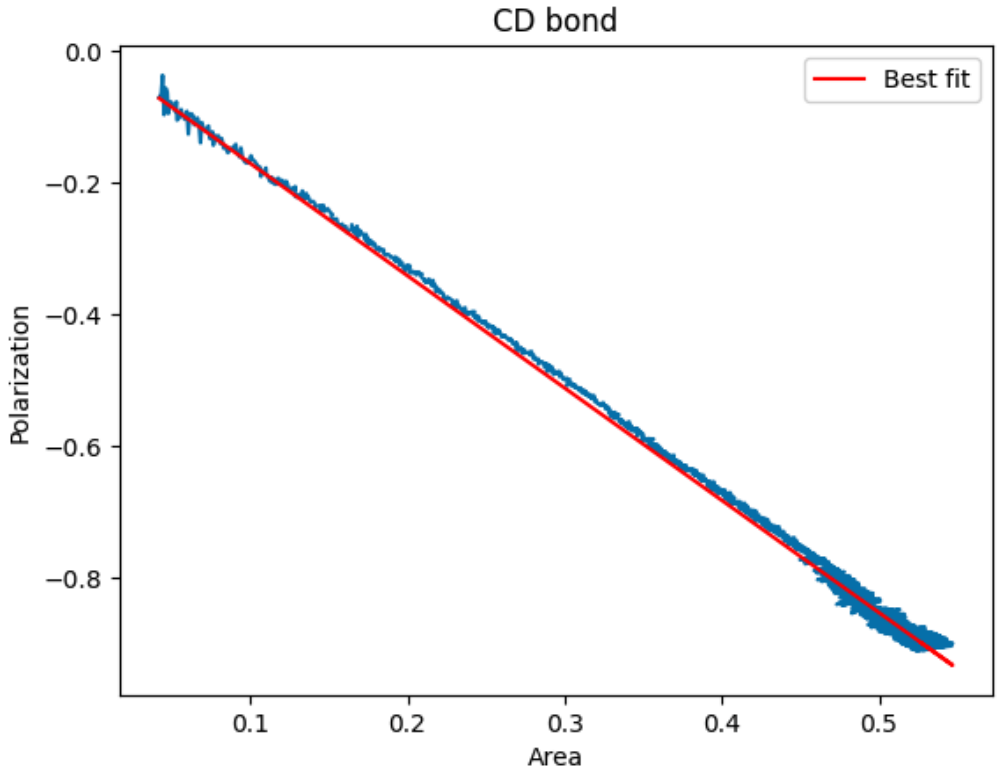




Fitting for calibration constant

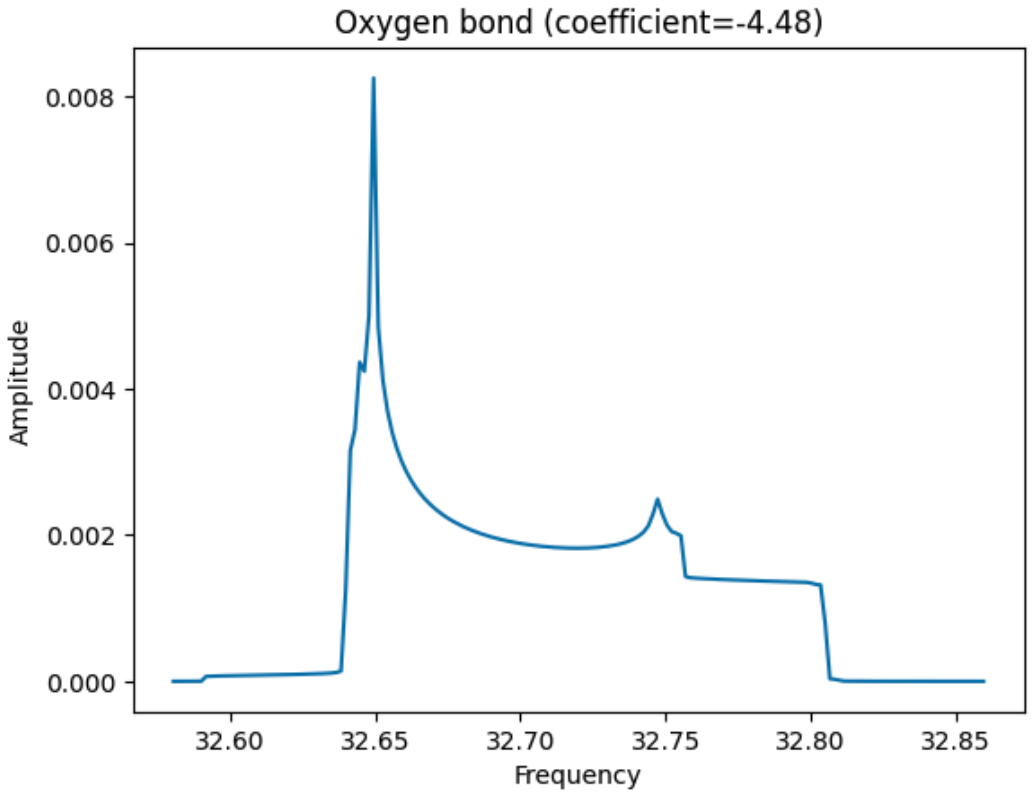


Calibration constant: **-4.48**

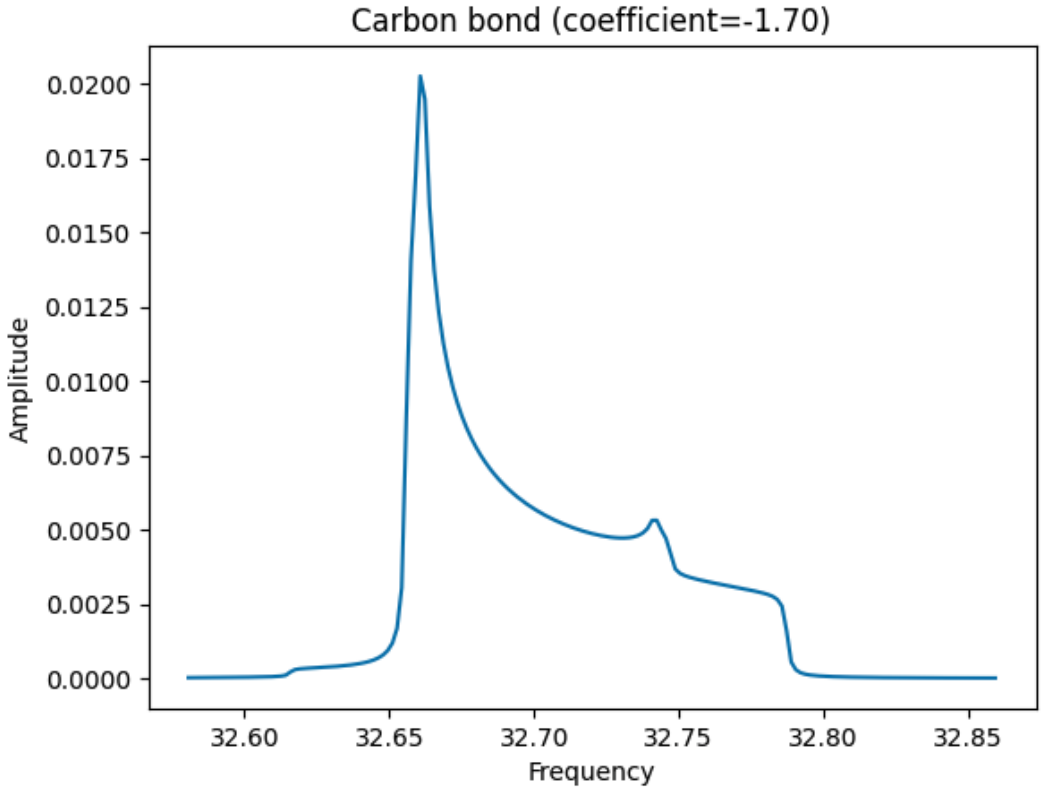


Calibration constant: **-1.7**

Comparing polarization from both methods

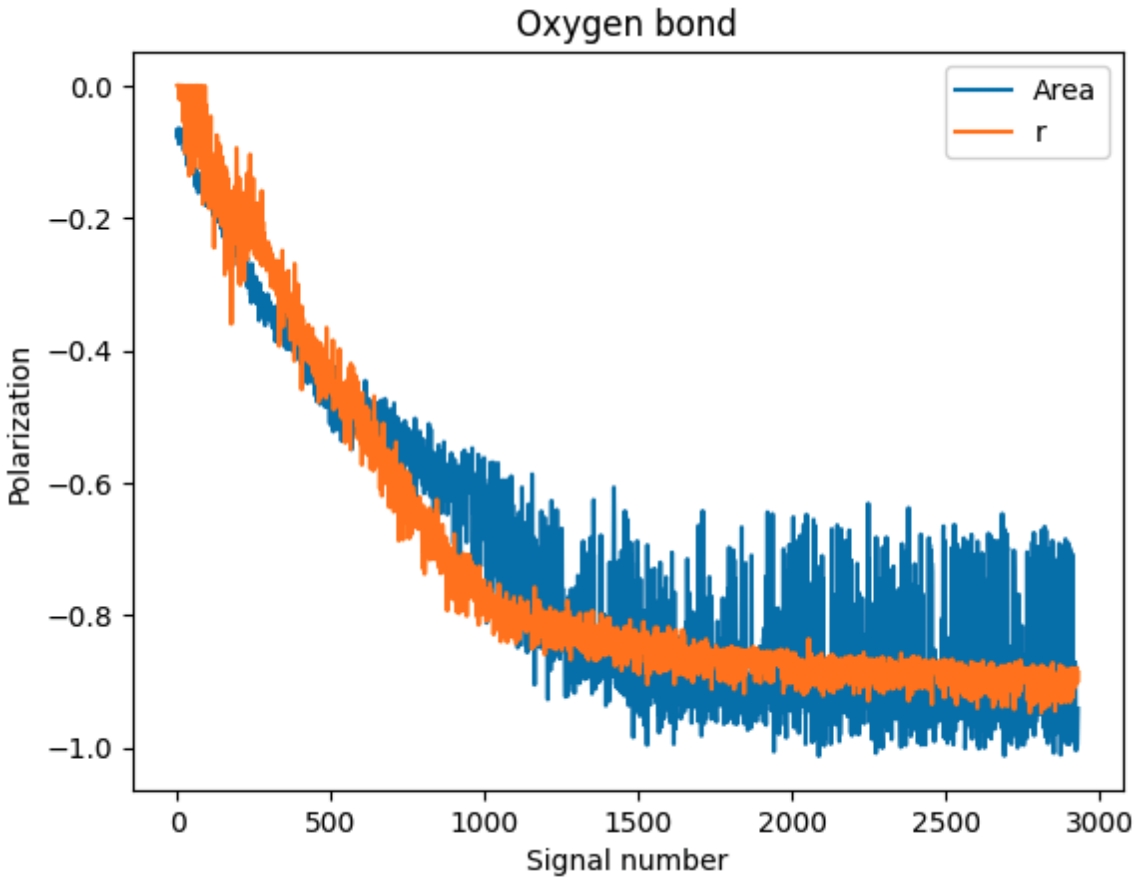


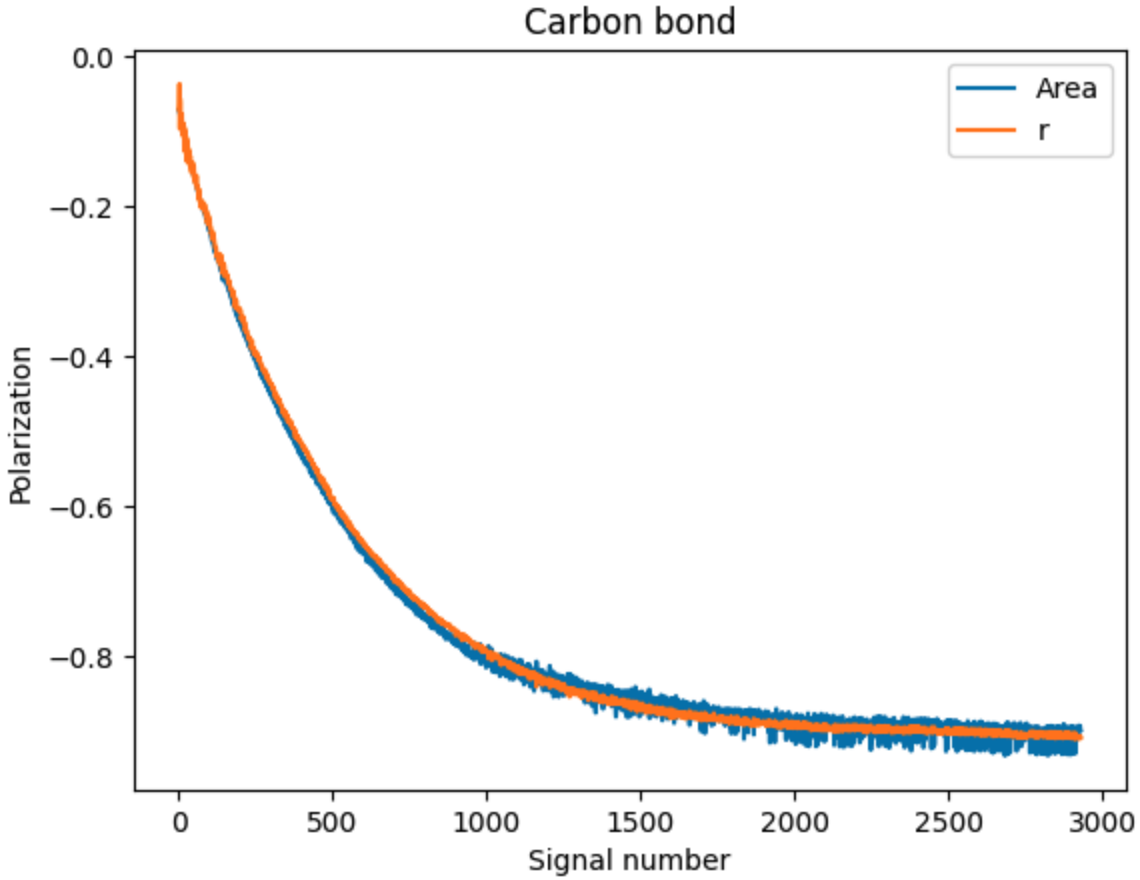
Polarization from area: **-98.66%**
Polarization from r: **-87.32%**



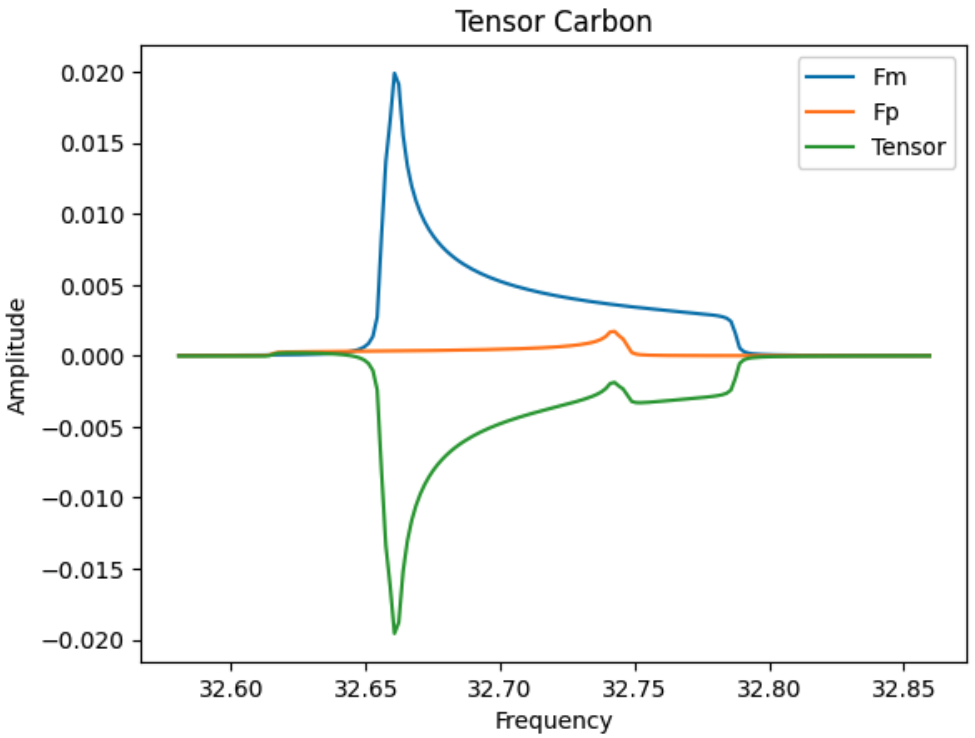
Polarization from area: **-88.49%**
Polarization from r: **-90.29%**

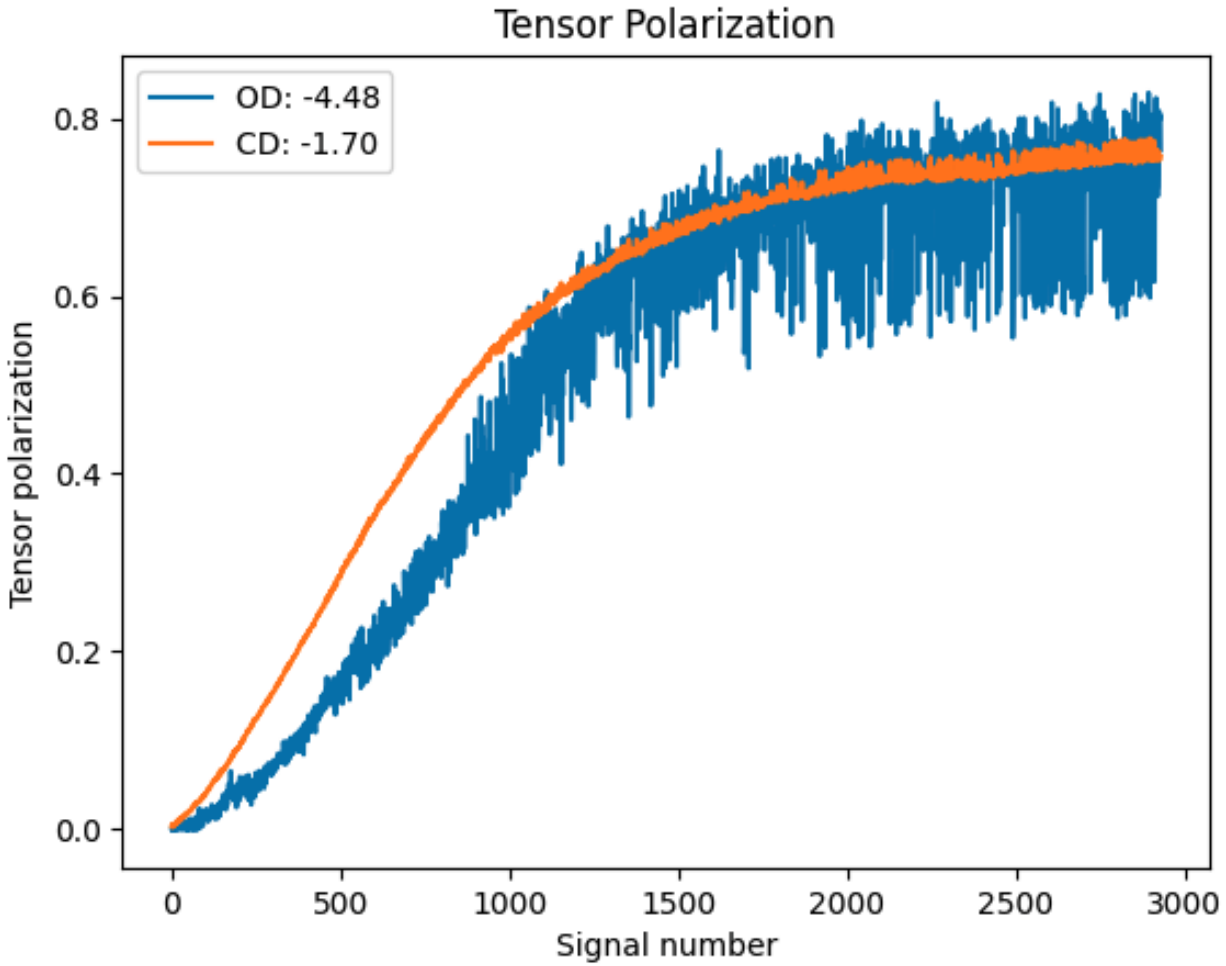
Polarization from area vs r parameter





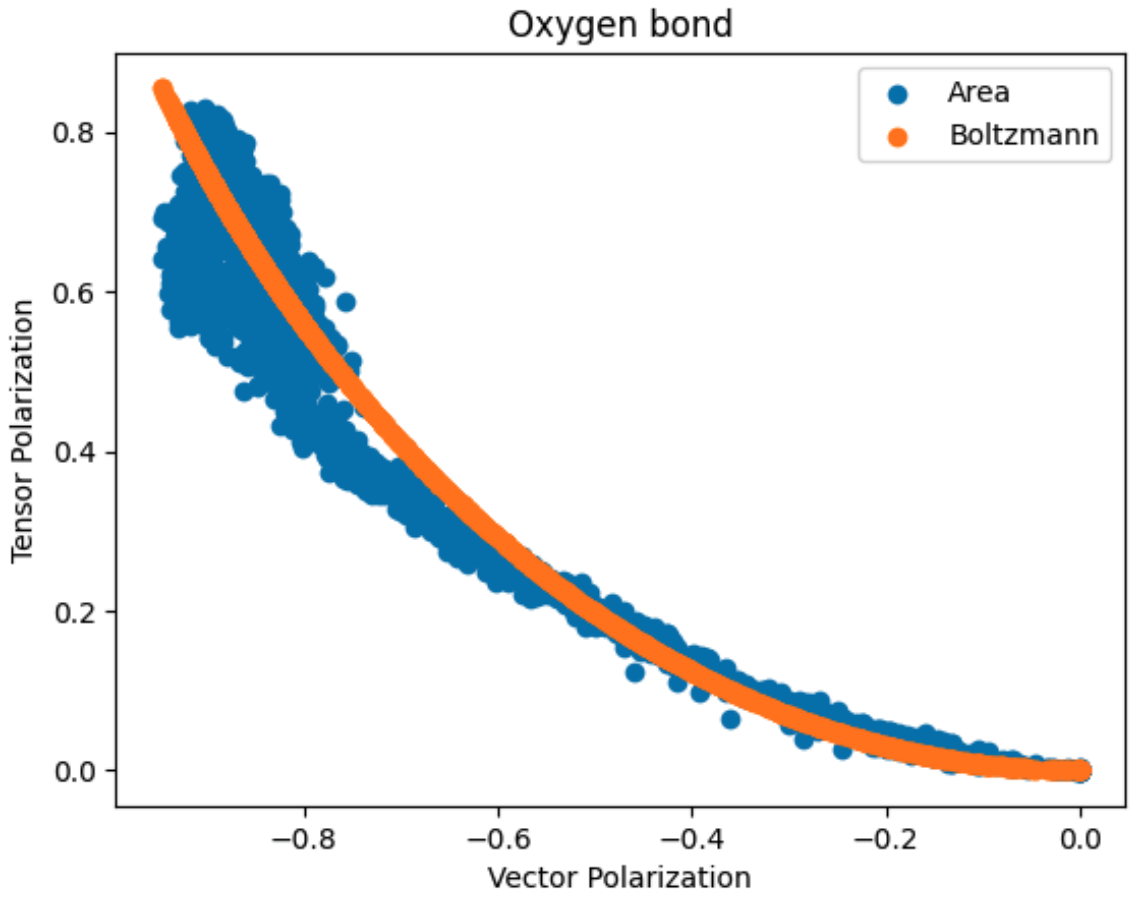
Tensor polarization

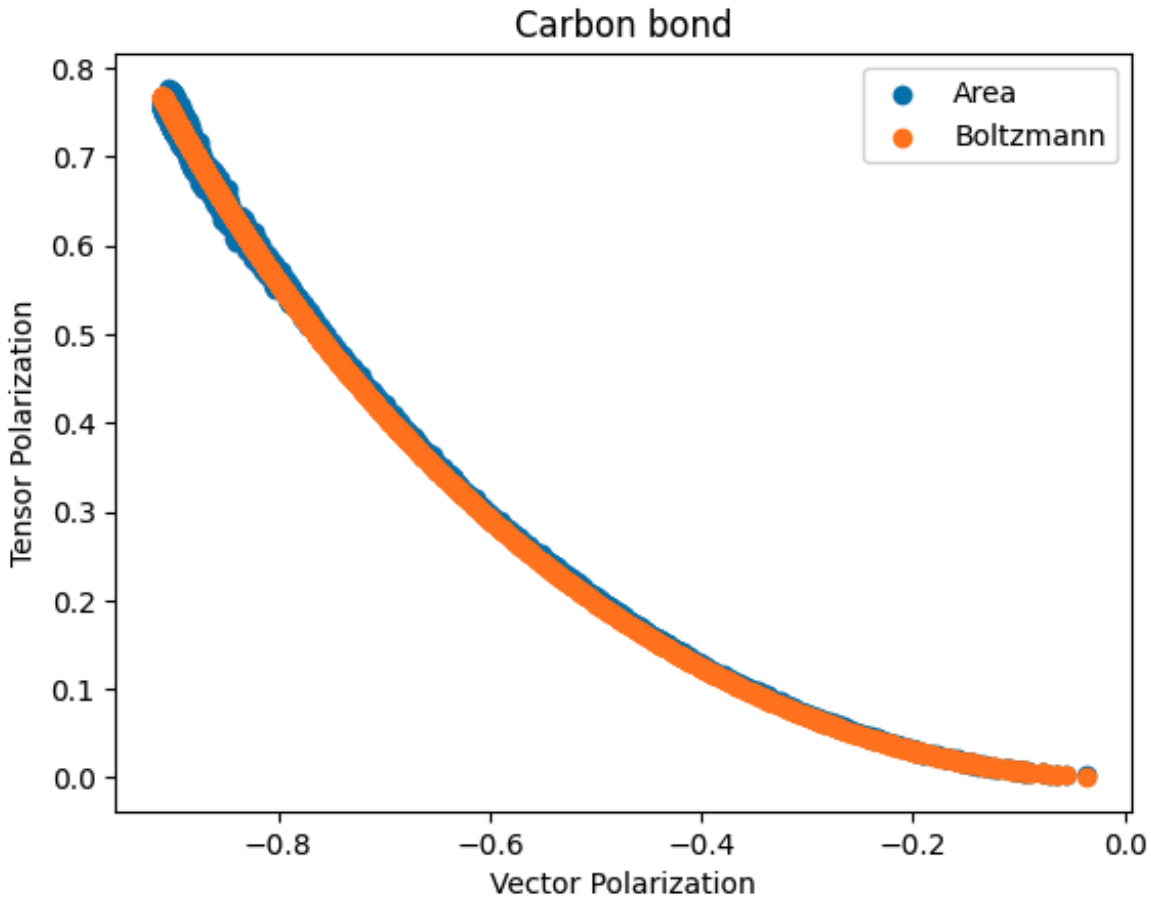




Boltzmann Distribution

$$Q = 2 - \sqrt{4 - 3P^2}$$





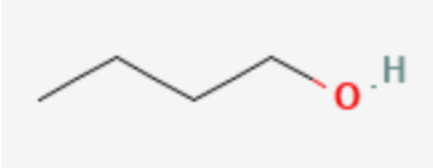
Conclusion

1. Polarized target group at UT
    1. Achieved 31.8mK!
    2. Adapt DNP apparatus for application in crystallography and nuclear physics experiments across multiple facilities
2. NMR analysis of deuterated propanediol
    1. Linear relationship between area and asymmetry parameter methods
    2. Quadratic relationship between tensor and vector polarization
    3. Both results support Boltzmann distribution for spin states at high polarization

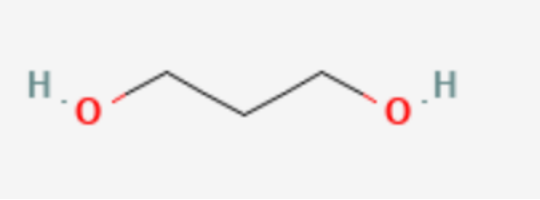
Back up slides

Vector polarization

- The paper investigated deuterated butanol, C4D9OD.



- We want to analyze deuterated propanediol, C3D8O2



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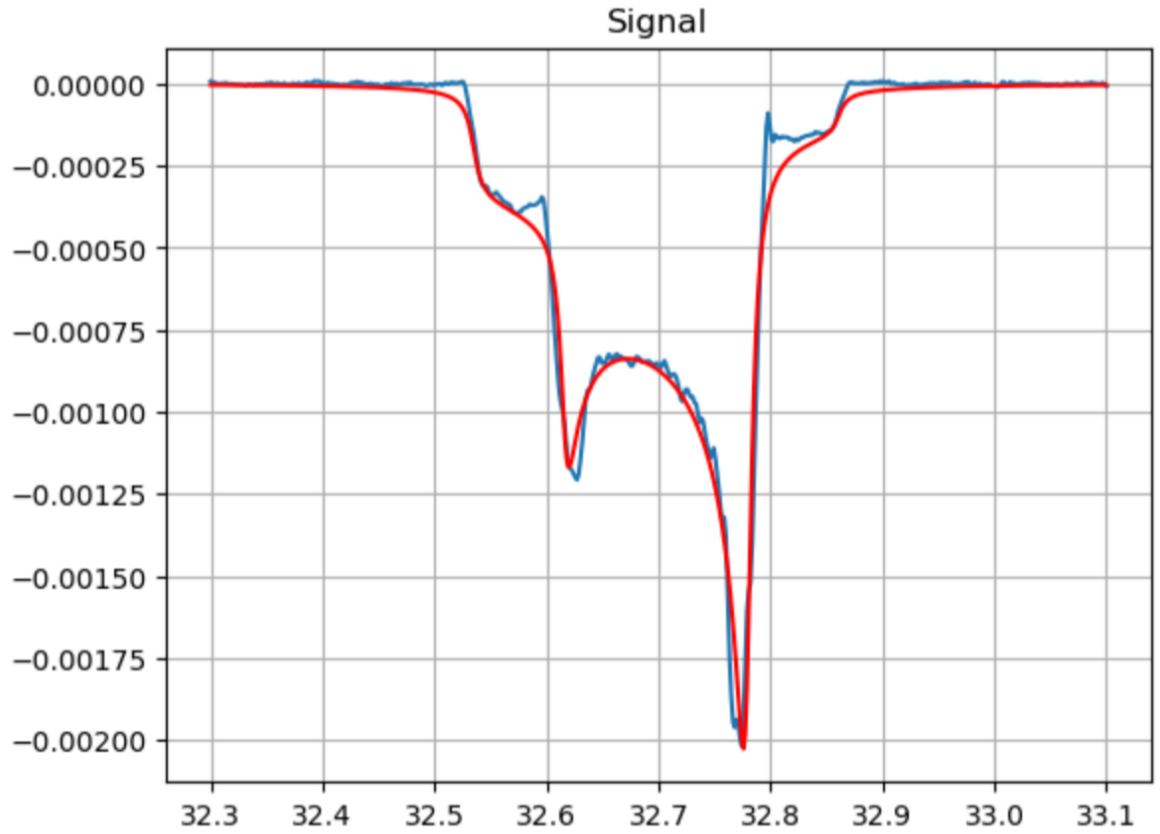
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

A line-shape analysis for spin-1 NMR signals

The Spin Muon Collaboration (SMC)

C. Dulya[a,b,*], D. Adams[c], B. Adeva[d], E. Arik[e], A. Arvidson[f], B. Badelek[f,g], M.K. Ballintijn[b,1], D. Bardin[2], G. Bardin[h], G. Baum[i], P. Berglund[j], L. Betev[k], I.G. Bird[h,3], R. Birsa[l], P. Björkholm[f], B.E. Bonner[c], N. de Botton[h], M. Boutemeur[m,4], F. Bradamante[l,5], A. Bressan[l,6], S. Bültmann[i,7], E. Burtin[h], C. Cavata[h], D. Crabb[n], J. Cranshaw[c,8], T. Çuhadar[e], S. Dalla Torre[l], R. van Dantzig[b], B. Derro[s], A. Deshpande[m], S. Dhawan[m], A. Dyring[f], S. Eichblatt[c,9], J.C. Faivre[h], D. Fasching[o,10], F. Feinstein[h], C. Fernandez[d,p], B. Frois[q,h], A. Gallas[d], J.A. Garzon[d,p], T. Gaussiran[c], R. Gehring[r], M. Giorgi[l], E. von Goeler[s], St. Goertz[r], F. Gomez[d], G. Gracia[d], N. de Groot[b,11], M. Grosse Perdekamp[a,12], E. Gülmez[c], J. Harmsen[r], D. von Harrach[t], T. Hasegawa[u,13], P. Hautle[q,14], N. Hayashi[u,15], C.A. Heusch[q,16], N. Horikawa[u], V.W. Hughes[m], G. Igo[a], S. Ishimoto[u,17], T. Iwata[v], E.M. Kabuß[t], T. Kageya[u], L. Kalinovskaya[w,18], A. Karev[w], H.J. Kessler[x], T.J. Ketel[b], A. Kishi[v], Yu. Kisselev[w], L. Klostermann[b,19], D. Krämer[j], V. Krivokhijine[w], W. Kröger[q,16], V. Kukhtin[w], K. Kurek[g], J. Kyynäräinen[q,j], M. Lamanna[l], U. Landgraf[x], J.M. Le Goff[h,q], F. Lehar[h], A. de Lesquen[h], J. Lichtenstadt[y], T. Lindqvist[f], M. Litmaath[b,5], M. Lowe[c,10], A. Magnon[h], G.K. Mallot[t], F. Marie[h], A. Martin[l], J. Martino[h], T. Matsuda[u,13], B. Mayes[p], J.S. McCarthy[b], K. Medved[w], W. Meyer[r], G. van Middelkoop[b], D. Miller[o], K. Mori[z], J. Moromisato[s], A. Nagaitsev[w],

Clean fit for deuterated ammonia (ND3)



Polarization: 53.894128263272236 %

```
[[Model]]
    Model(FitFunc)
[[Fit Statistics]]
    # fitting method   = leastsq
    # function evals   = 120
    # data points      = 512
    # variables        = 7
    chi-square         = 1.5933e-06
    reduced chi-square = 3.1551e-09
    Akaike info crit   = -10015.0668
    Bayesian info crit = -9985.39850
    R-squared          = 0.98528332
##  Warning: uncertainties could not be estimated:
[[Variables]]
    A:   -0.07454608 (init = 0.0468)
    G:   -2.8006e-05 (init = -1e-05)
    r:    2.50264629 (init = 1.1)
    wQ:   0.02718309 (init = 0.027)
    wL:   32.6978501 (init = 32.7)
    eta: -0.03122776 (init = 0.5)
    xi:   0.00498219 (init = -0.0012)
```

https://github.com/jdmax/NMR_Analysis

LMFIT and scipy.optimize packages

- Non-linear Least-squares Minimization and Curve-Fitting for Python (LMFIT) builds on and expands on many of the optimization methods of scipy.optimize.
- Scipy.optimize rovides functions to minimize, or maximize, objective functions. Including olvers for non-linear problems (with support for local and global optimization), linear programming, constrained and non-linear least squares, root finding, and curve fitting.
- LMFIT builds on this with the creation of Parameter objects, a Model class, allowing for quick change of optimization method, and improved confidence intervals.

(13) Parameters from paper

- w_d - Larmor frequency, in this case deuteron. 30.7MHz/T
- η - filling factor of coil
- $\mathcal{K}$ - contains all unknown frequency-dependent gains in the Q-meter; found from TE calibration.
- w_q - quadruple interaction. $\hbar w_q = eq * eQ/8$
- R - dimensionless parameter $R = \frac{w - w_d}{3w_q}$
- r - asymmetry parameter $r = e^{\beta \hbar w_d}$, $\beta = \frac{1}{K_B T}$
- a_{0-3} - fitting coefficients for 3rd order polynomial of signal wings
- ξ - false asymmetry from q-meter distortions
- $\mathcal{L}$ - constant gain factor of q-meter
- $\sigma = 3w_q A$ – dipolar broadening
- K - relative amount of O-D bonds to C-D bonds

Parameters in the code

- w – not a parameter, it is the frequency
- A– width of dipolar broadening
- G – scaling parameter
- r – asymmetry parameter
- w_q - quadruple interaction
- w_L - Larmor frequency
- eta (η)– peak width factor
- xi (ξ)- false asymmetry

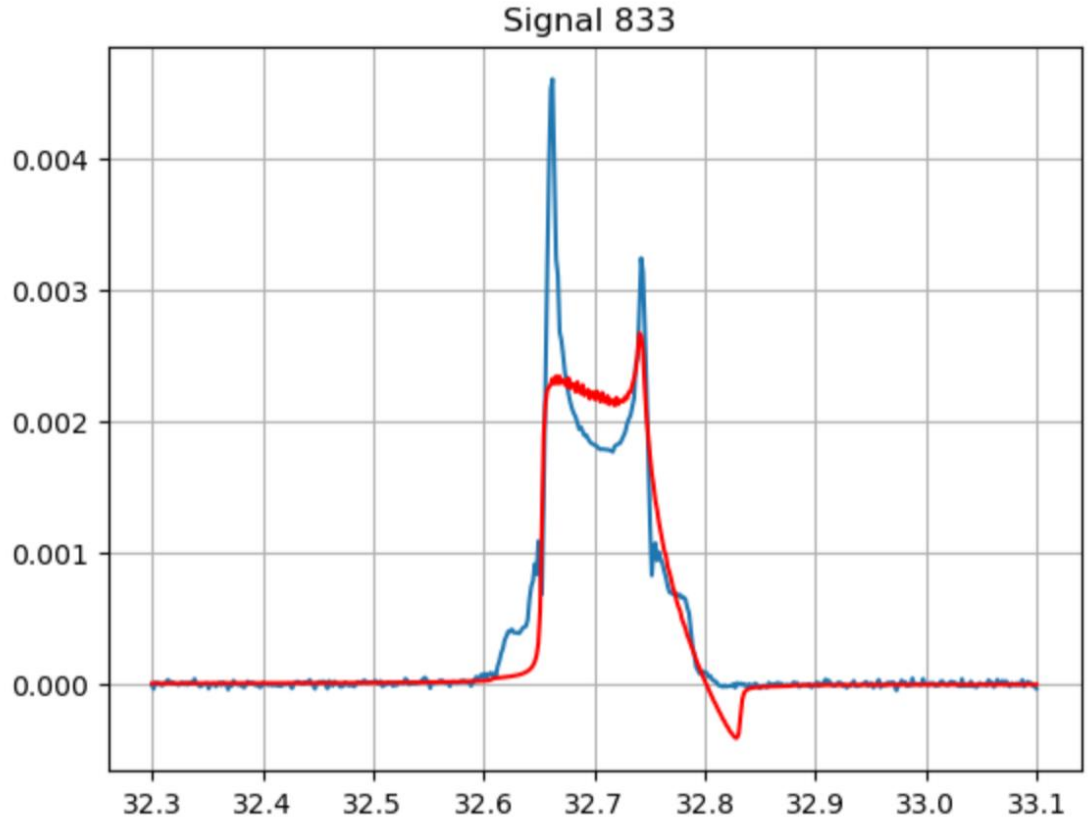
*Deuterated propanediol, C3D8O2 *

Fitting Function and bonds

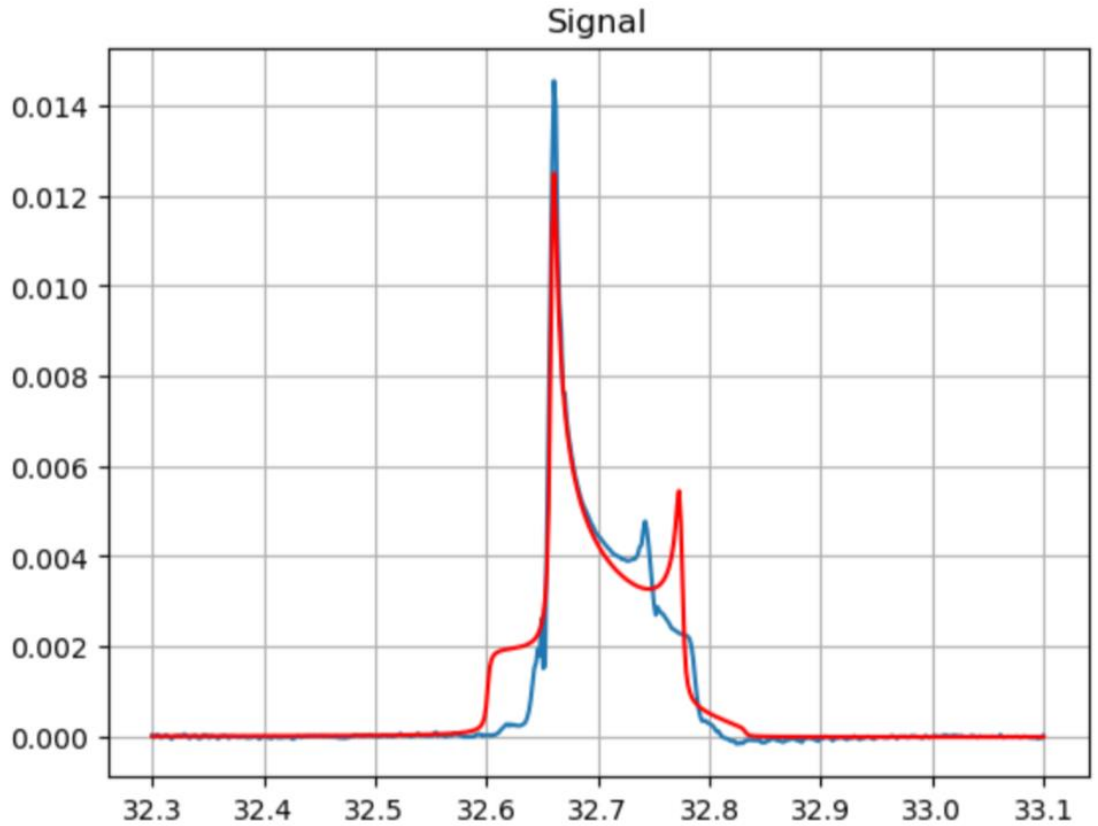
```
def SumFitFunc(w, A, G1, r, wQ1, wL1, eta1, xi1, G2, wQ2, wL2, eta2, xi2, K):
    OD = FitFunc(w, A, G1, r, wQ1, wL1, eta1, xi1)
    CD = FitFunc(w, A, G2, r, wQ2, wL2, eta2, xi2) #r could be the same
    signal = (1-K)*CD+K*OD
    return signal
```

- FitFunc describes the NMR signal for a single bond.
- The parameters labeled with “subscript” 1 are those related to the oxygen and deuteron bond. Those with subscript 2 are those related to the carbon and deuteron bond.
- Looking at the propanediol molecule, there are more carbon bonds and is therefore the stronger signal.
- The parameter K takes care of scaling the signals. K=.25

Fitting signal only one bond

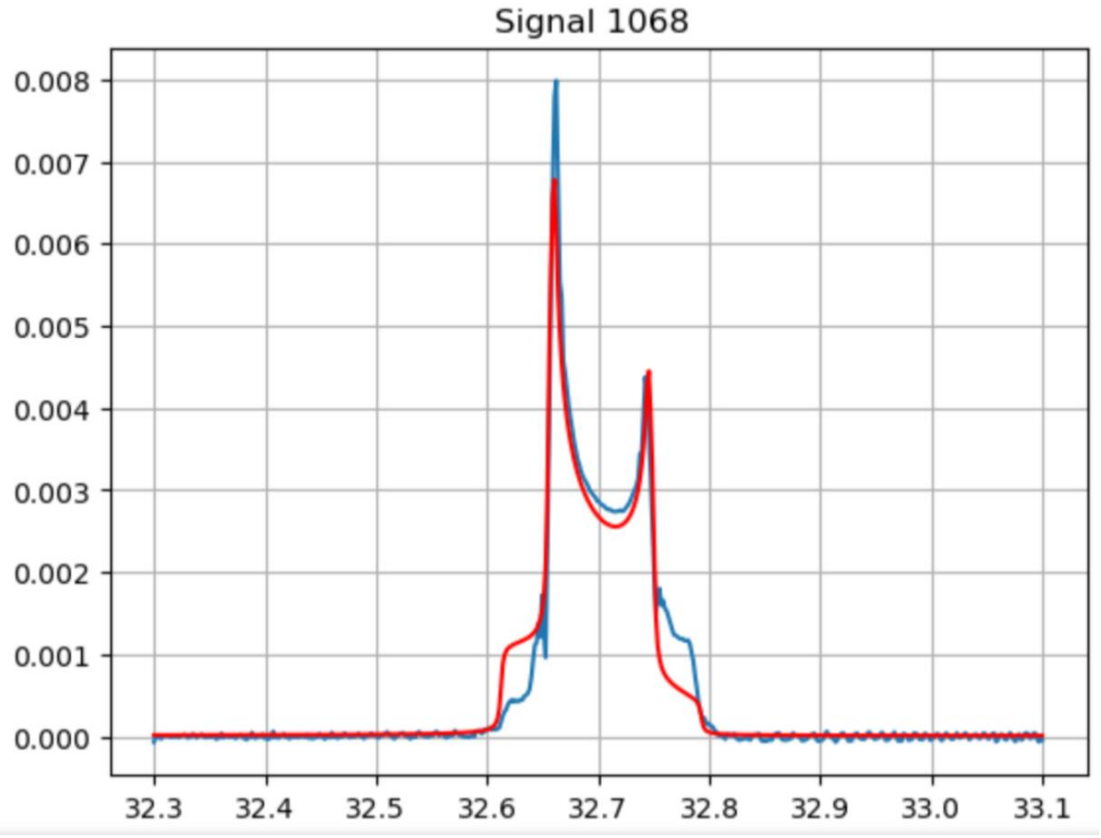


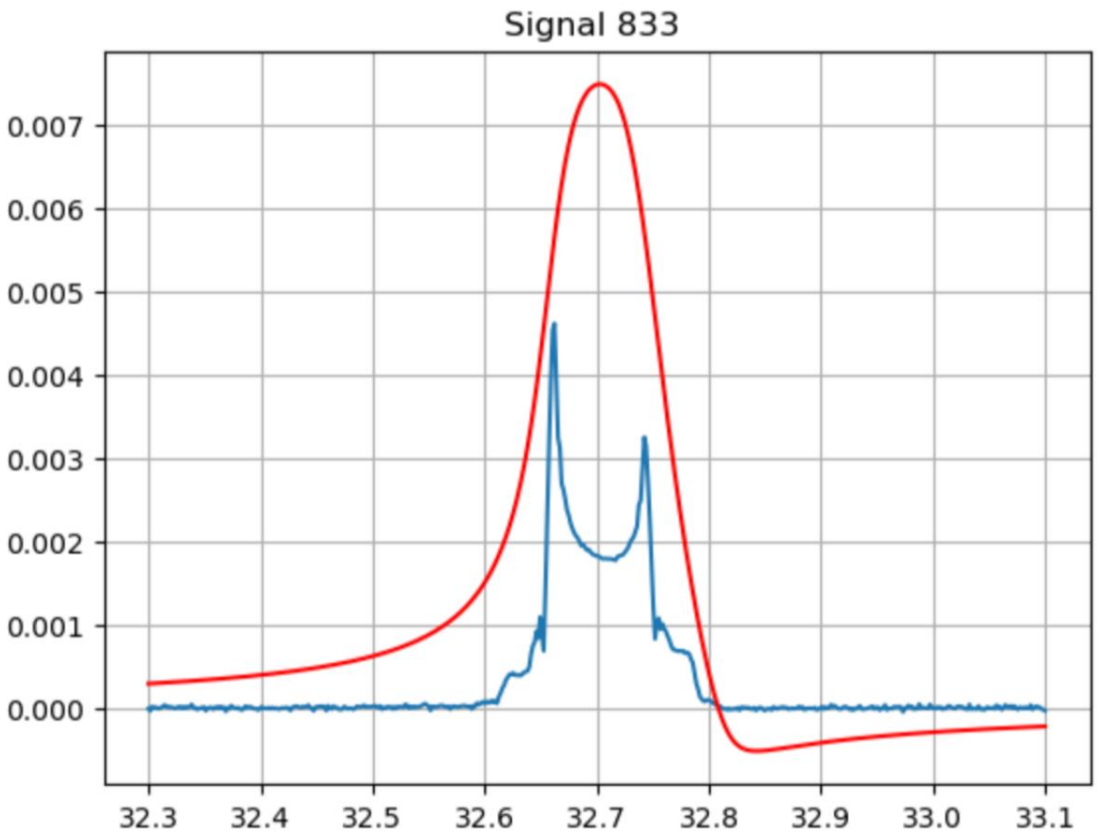
Polarization: -2.4001311126825025 %



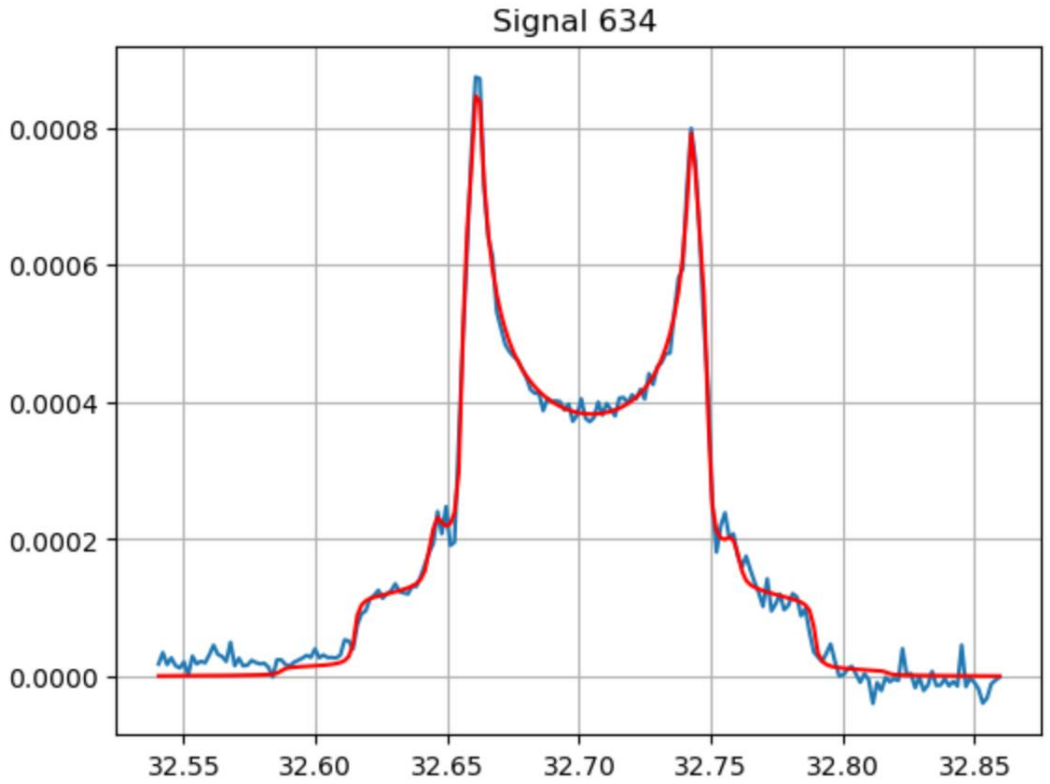
Polarization: 0.6975772654363473 %

Fitting signal two bonds





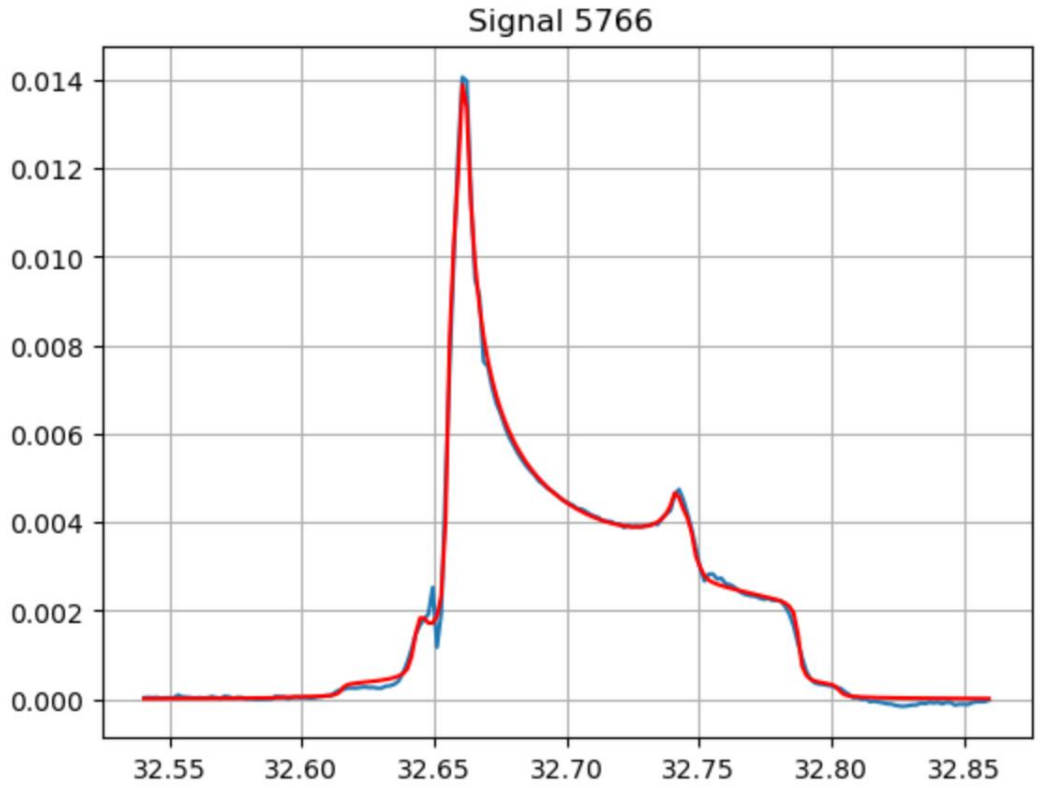
Clean low polarization fit



Polarization: -5.0550481394869315 %

```
[[Fit Statistics]]
    # fitting method   = leastsq
    # function evals   = 20631
    # data points      = 200
    # variables        = 12
    chi-square         = 6.6264e-08
    reduced chi-square = 3.5247e-10
    Akaike info crit   = -4341.58750
    Bayesian info crit = -4302.00769
    R-squared          = 0.99292920
[[Variables]]
    A:     0.02376276 +/- 0.00215068 (9.05%) (init = 0.01)
    G1:   -9.4556e-05 +/- 3.9380e-05 (41.65%) (init = -0.0001)
    r:     0.92691028 +/- 0.03097287 (3.34%) (init = 0.2)
    wQ1:   0.01914866 +/- 1.7967e-04 (0.94%) (init = 0.021)
    wL1:   32.7019698 +/- 5.5449e-04 (0.00%) (init = 32.703)
    eta1:  0.03000000 +/- 0.24858201 (828.61%) (init = 0.02)
    xi1:  -0.26234451 +/- 0.14799693 (56.41%) (init = -0.002)
    G2:   -7.5154e-05 +/- 3.3850e-05 (45.04%) (init = -7e-05)
    wQ2:   0.01453920 +/- 2.0624e-05 (0.14%) (init = 0.014)
    wL2:   32.7021501 +/- 6.3896e-05 (0.00%) (init = 32.702)
    eta2:  0.07021558 +/- 0.00200227 (2.85%) (init = 0.075)
    xi2:  -0.04117382 +/- 0.02775526 (67.41%) (init = -0.002)
    K:     0.1 (fixed)
```

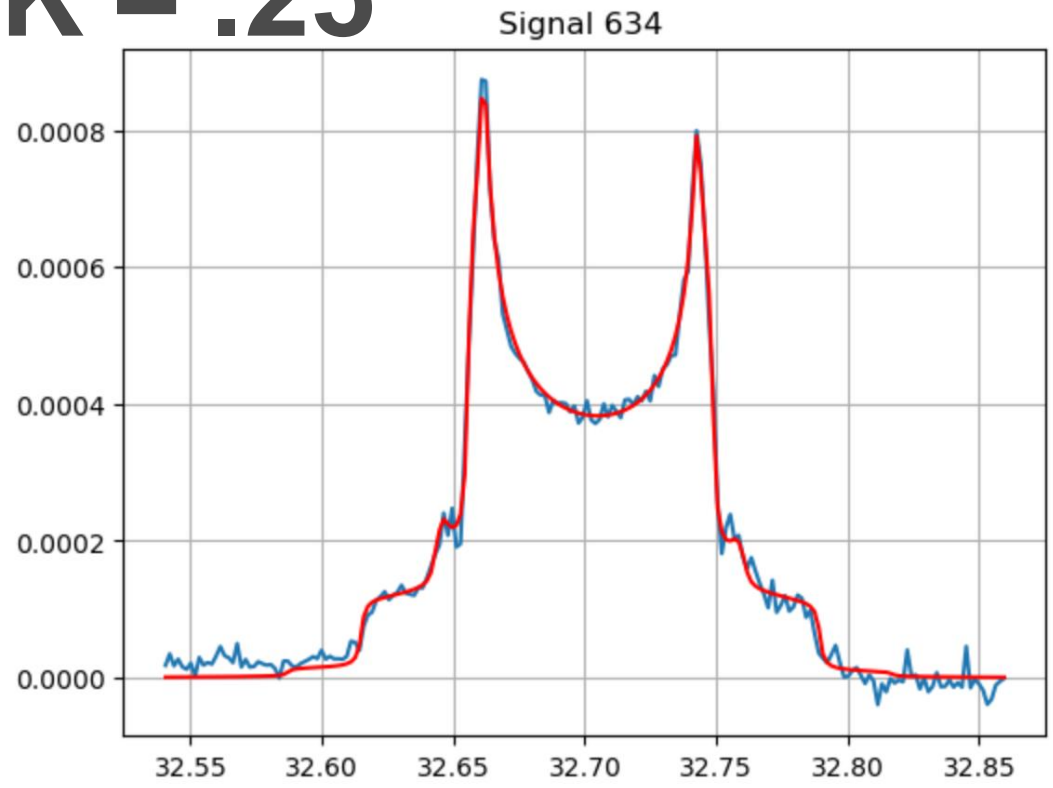
High polarization

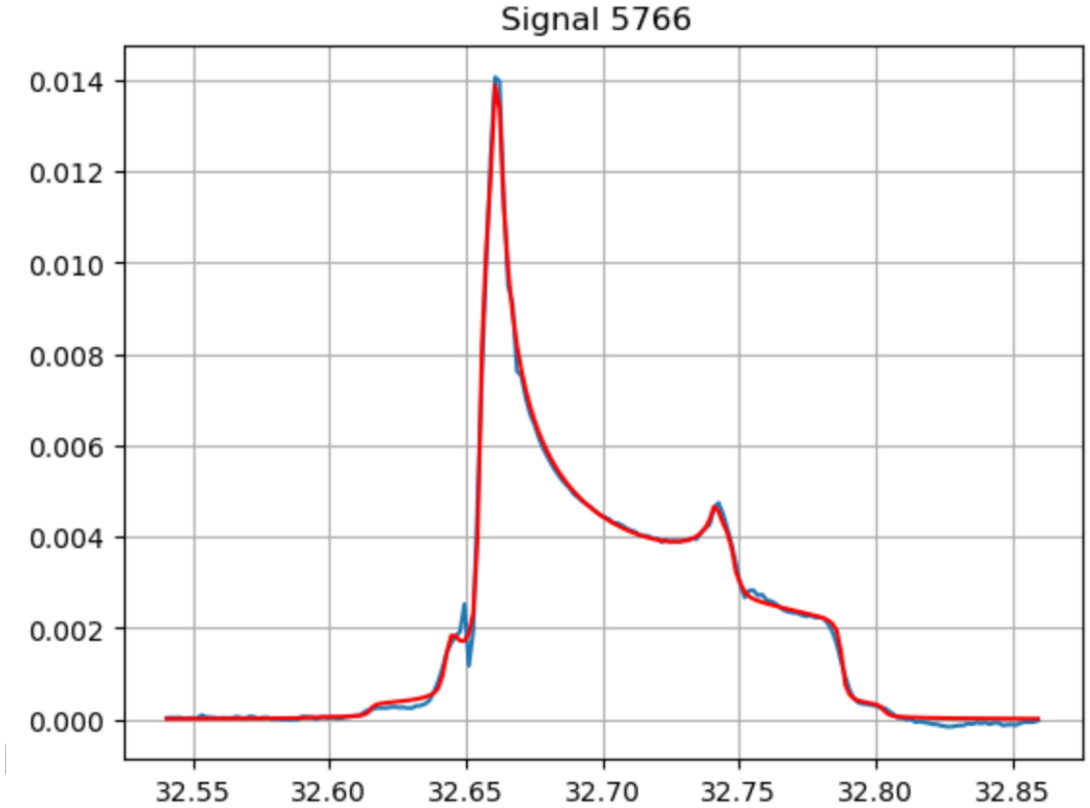


Polarization: -84.82248101733923 %

```
[[Fit Statistics]]
    # fitting method   = leastsq
    # function evals   = 1028
    # data points      = 200
    # variables        = 12
    chi-square         = 5.0057e-06
    reduced chi-square = 2.6626e-08
    Akaike info crit   = -3476.64905
    Bayesian info crit = -3437.06924
    R-squared          = 0.99671566
[[Variables]]
    A:     0.02355381 +/- 0.00146598 (6.22%) (init = 0.01)
    G1:   -4.2540e-05 +/- 3.3962e-06 (7.98%) (init = -0.0001)
    r:     0.13764835 +/- 0.00666425 (4.84%) (init = 0.2)
    wQ1:   0.01771119 +/- 1.9275e-04 (1.09%) (init = 0.021)
    wL1:   32.6967425 +/- 6.2361e-04 (0.00%) (init = 32.703)
    eta1:  0.02999997 +/- 0.14917215 (497.24%) (init = 0.02)
    xi1:   0.63355134 +/- 0.32741855 (51.68%) (init = -0.002)
    G2:   -5.0550e-05 +/- 8.1991e-07 (1.62%) (init = -7e-05)
    wQ2:   0.01438662 +/- 2.9686e-05 (0.21%) (init = 0.014)
    wL2:   32.7013952 +/- 9.0476e-05 (0.00%) (init = 32.702)
    eta2:  0.07513548 +/- 0.00135807 (1.81%) (init = 0.075)
    xi2:  -0.04704491 +/- 0.02473496 (52.58%) (init = -0.002)
    K:     0.1 (fixed)
```

K = .25





= 0.01)

Polarization: -5.017684001201892 %

= -0.000

r:	0.92743141	+/- 0.03098974	(3.34%) (init = 0.2)
wQ1:	0.01914885	+/- 1.7955e-04	(0.94%) (init = 0.021)
wL1:	32.7019717	+/- 5.5410e-04	(0.00%) (init = 32.703)
eta1:	0.03000000	+/- 0.05409371	(180.31%) (init = 0.02)
xi1:	-0.26115484	+/- 0.14814271	(56.73%) (init = -0.002
G2:	-9.0873e-05	+/- 4.1226e-05	(45.37%) (init = -7e-05
wQ2:	0.01453921	+/- 2.0623e-05	(0.14%) (init = 0.014)
wL2:	32.7021503	+/- 6.3892e-05	(0.00%) (init = 32.702)
eta2:	0.07021579	+/- 0.00200218	(2.85%) (init = 0.075)
xi2:	-0.04153692	+/- 0.02774471	(66.80%) (init = -0.002
K:	0.25 (fixed)		

0.01)

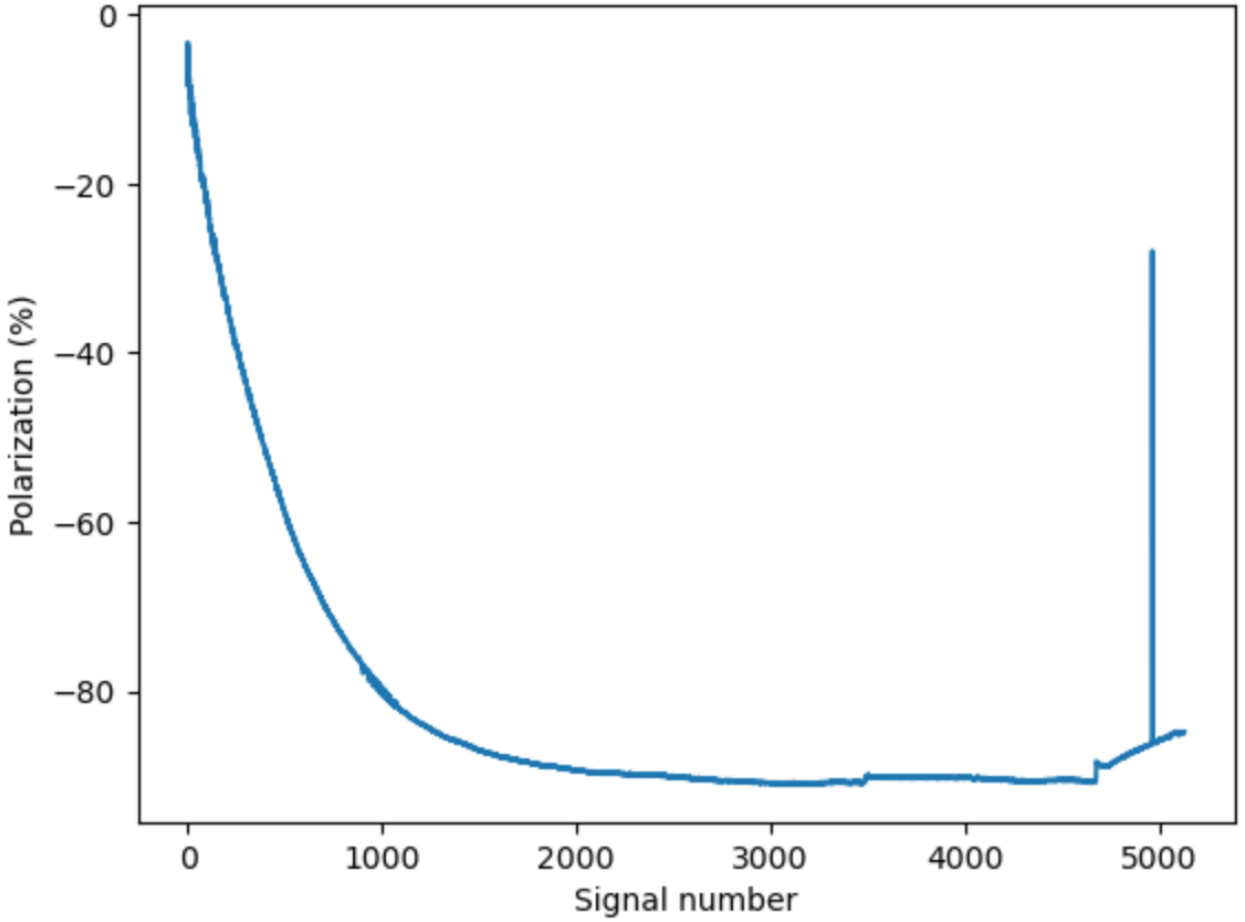
Polarization: -84.82250473752583 %

-0.0001)

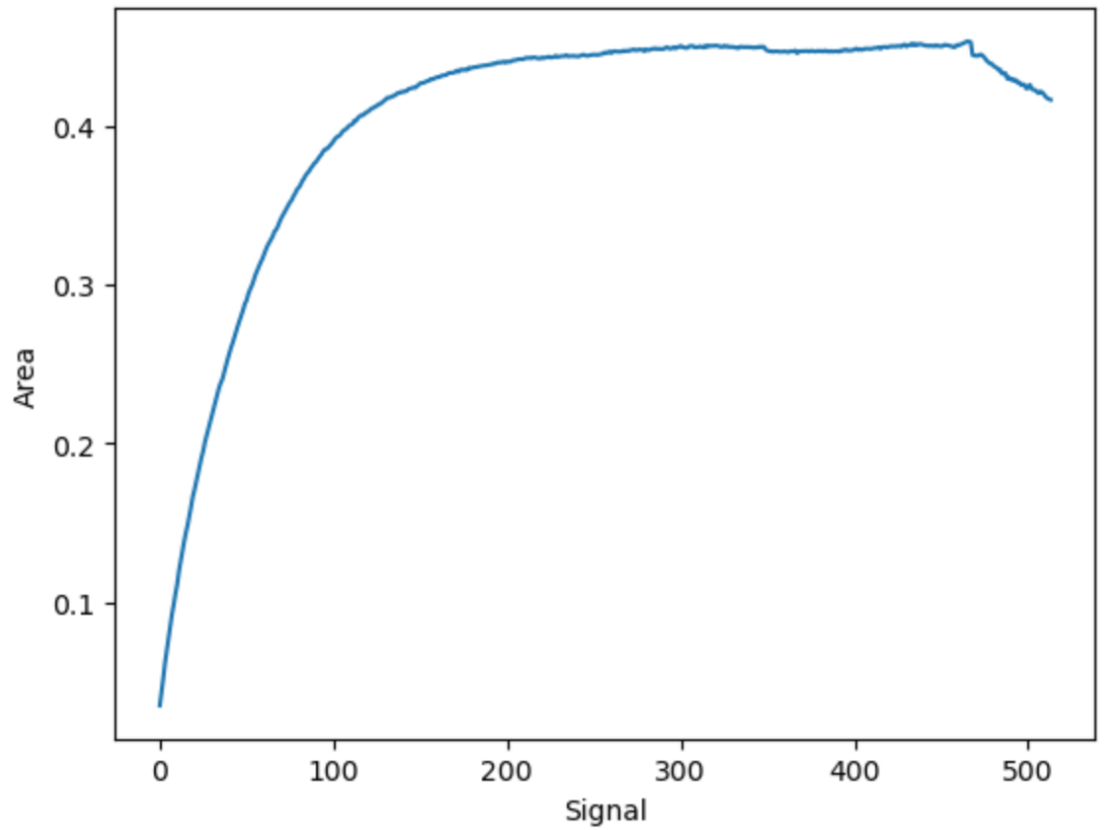
r:	0.13764815	+/- 0.00666425	(4.84%) (init = 0.2)
wQ1:	0.01771118	+/- 1.9275e-04	(1.09%) (init = 0.021)
wL1:	32.6967425	+/- 6.2361e-04	(0.00%) (init = 32.703)
eta1:	0.03000000	+/- 0.22231844	(741.06%) (init = 0.02)
xi1:	0.63356462	+/- 0.32742153	(51.68%) (init = -0.002)
G2:	-6.0661e-05	+/- 9.8389e-07	(1.62%) (init = -7e-05)
wQ2:	0.01438662	+/- 2.9686e-05	(0.21%) (init = 0.014)
wL2:	32.7013952	+/- 9.0475e-05	(0.00%) (init = 32.702)
eta2:	0.07513552	+/- 0.00135807	(1.81%) (init = 0.075)
xi2:	-0.04704547	+/- 0.02473511	(52.58%) (init = -0.002)
K:	0.25 (fixed)		

Polarization v Time

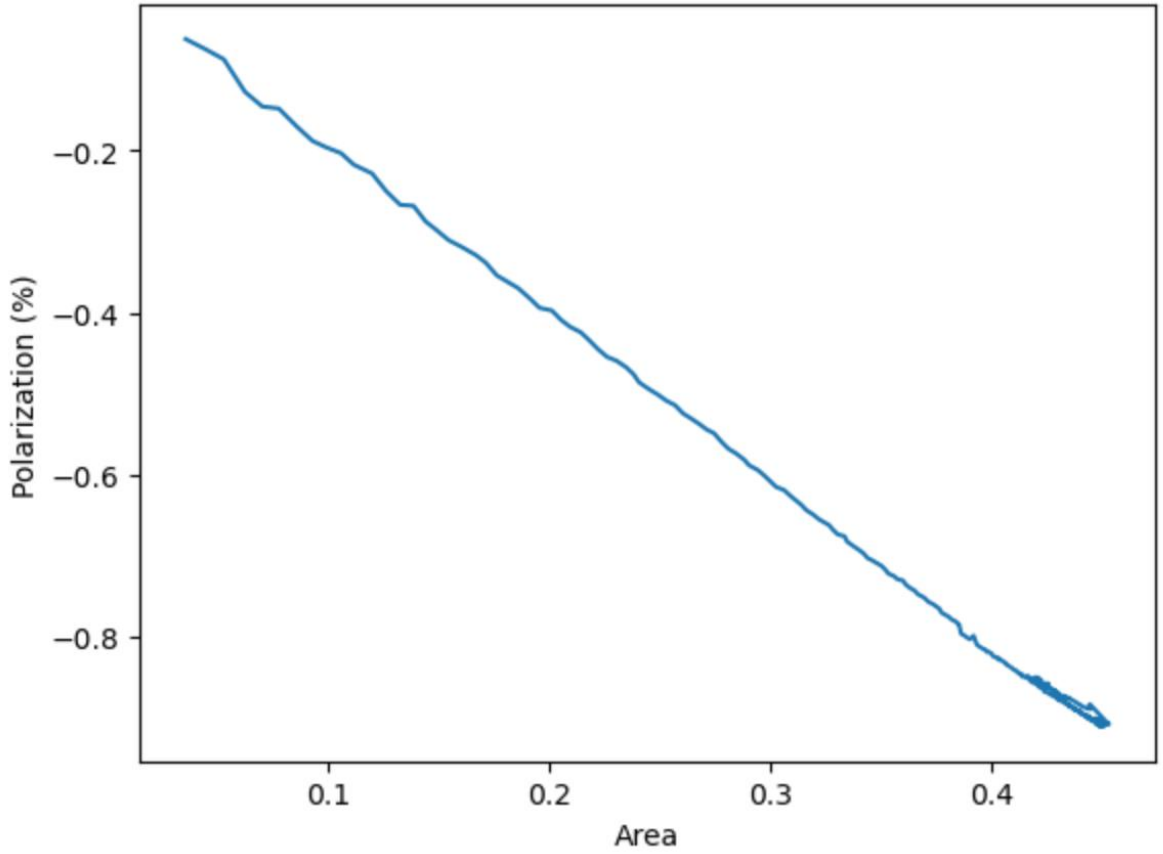
Having ”good” fits, we can track polarization over time

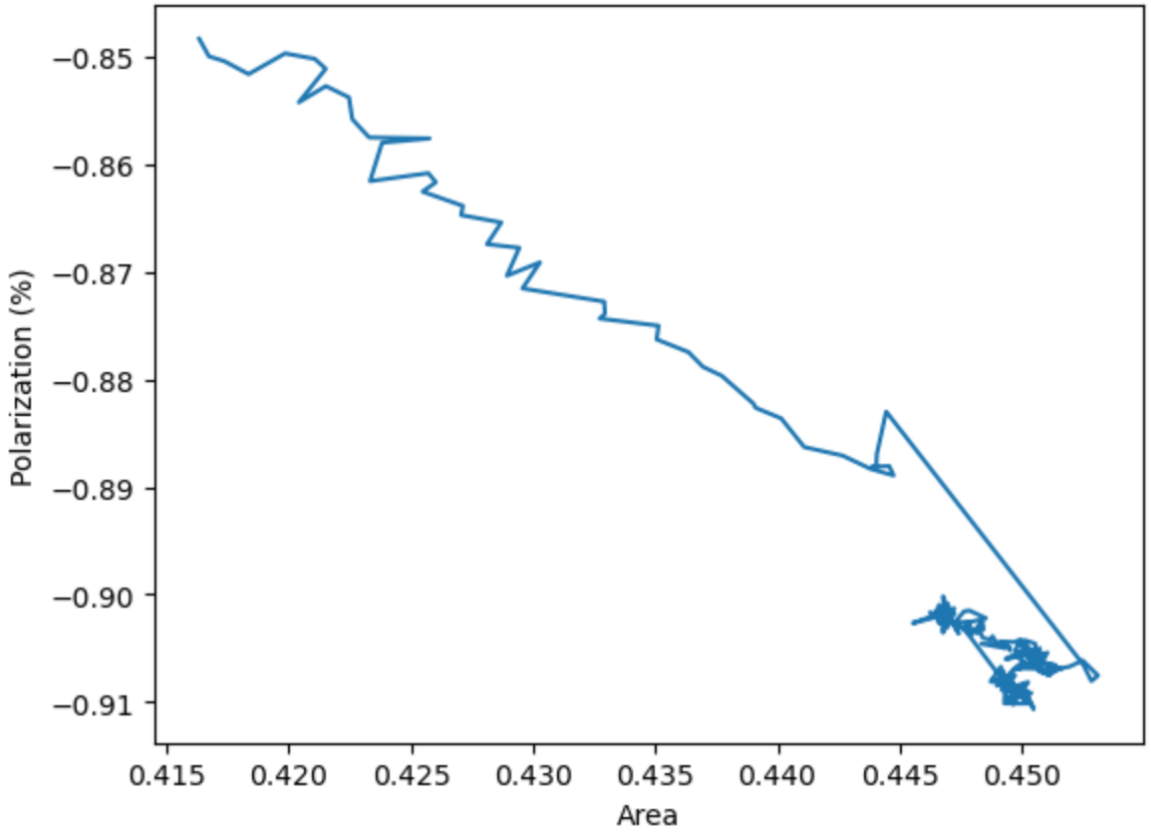


Area v Time (every 10 signals)

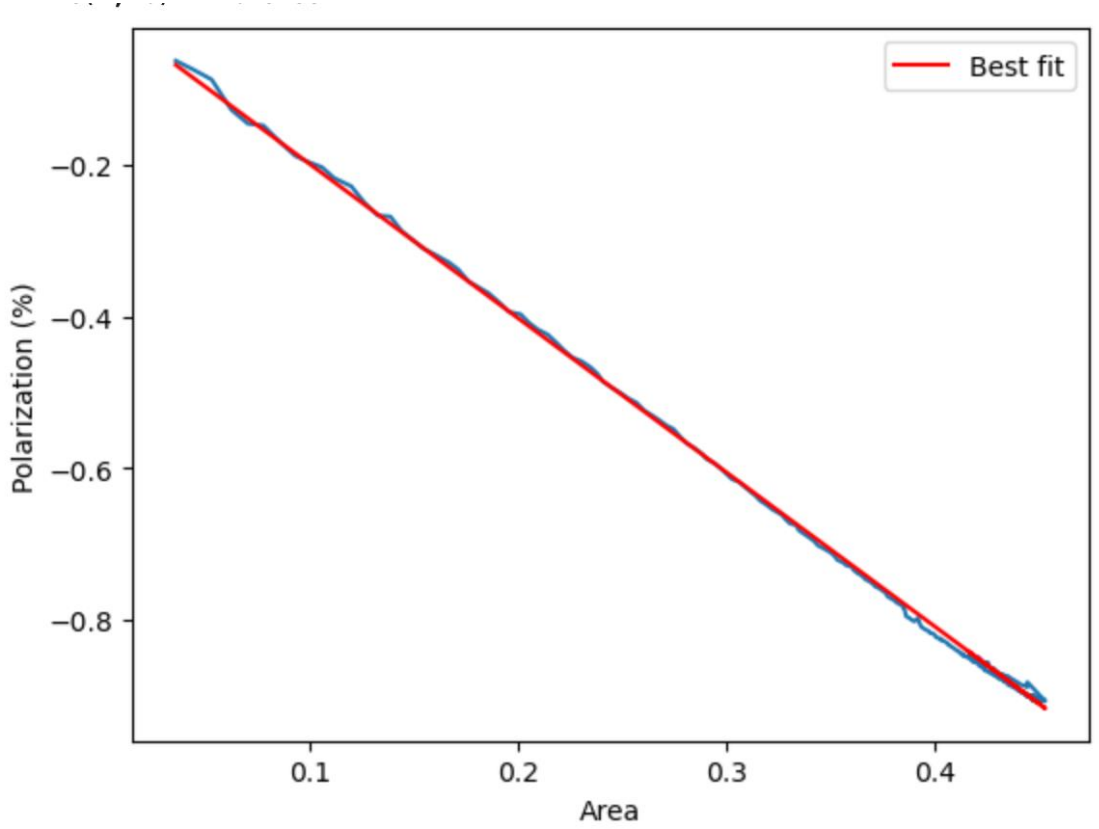


Polarization (%) v Area





Linear fit of polarization vs area



- This tells us that Boltzmann distribution appears to hold even at high vector polarization.
- However, we want to test each individual bond of propanediol.