

Enhancing the modulation depth and sensitivity in PELDOR experiments at 94 GHz

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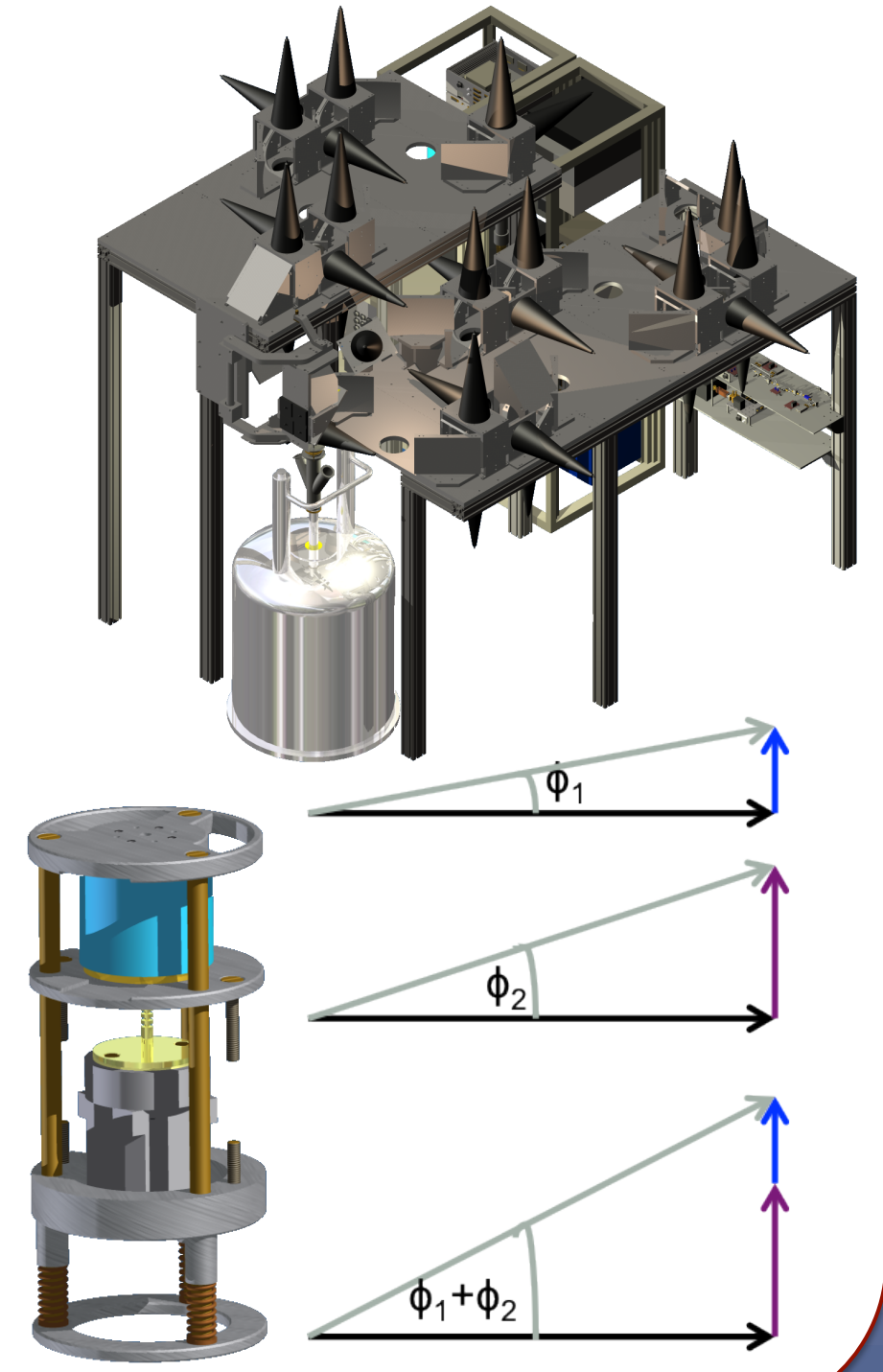
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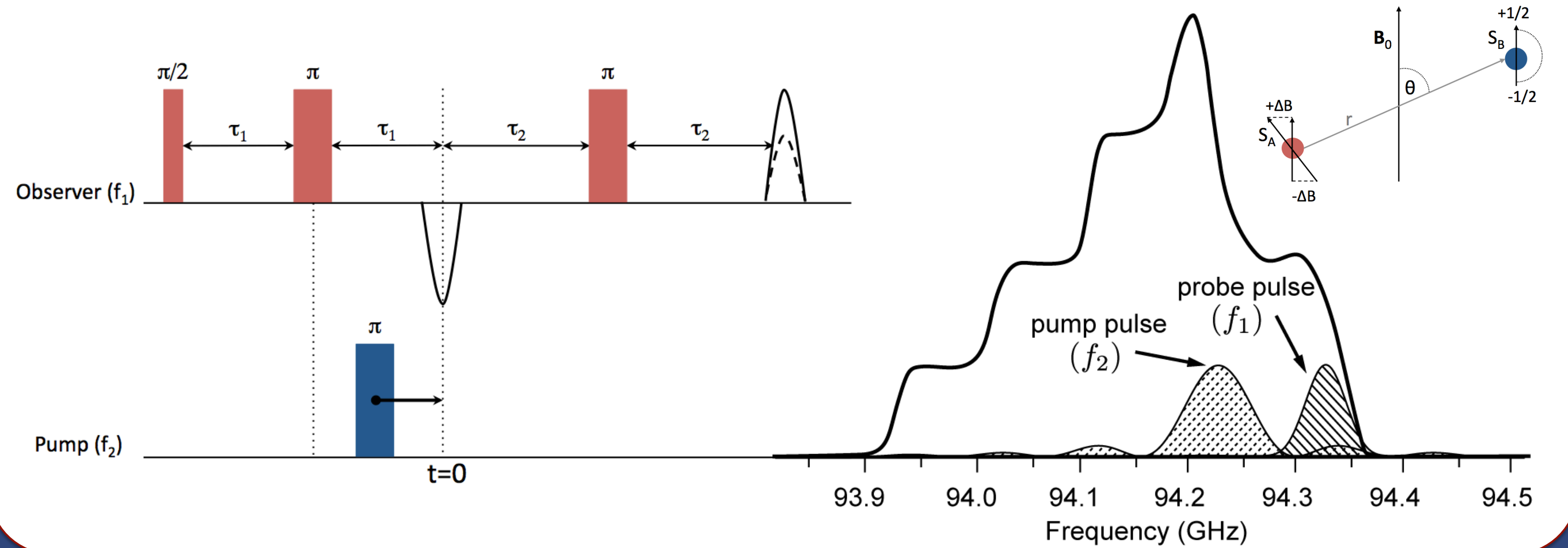
HiPER^[2]: 1kW Pulsed EPR at 94 GHz

- Non-resonant cavity, 1 GHz instantaneous bandwidth, 4.5ns $\pi/2$.
- High concentration sensitivity, large sample volume
- 4-channel 16 state vector modulator phase control for Composite Pulses
- First demonstration of Composite Pulses at W-band
- Improved modulation depth in PELDOR using such compensation pulses.



Pulsed ELDOR for distance measurements

Pulses of different frequencies excite separate parts of the spectrum. A refocused echo is performed on one set of spins (observer) while a second set is inverted, creating a local magnetic field that modulates the echo via dipolar coupling. The modulation is dependent on the fraction F_B of pump spins excited. In high field experiments, it is difficult to excite large populations of spins due to broadening.

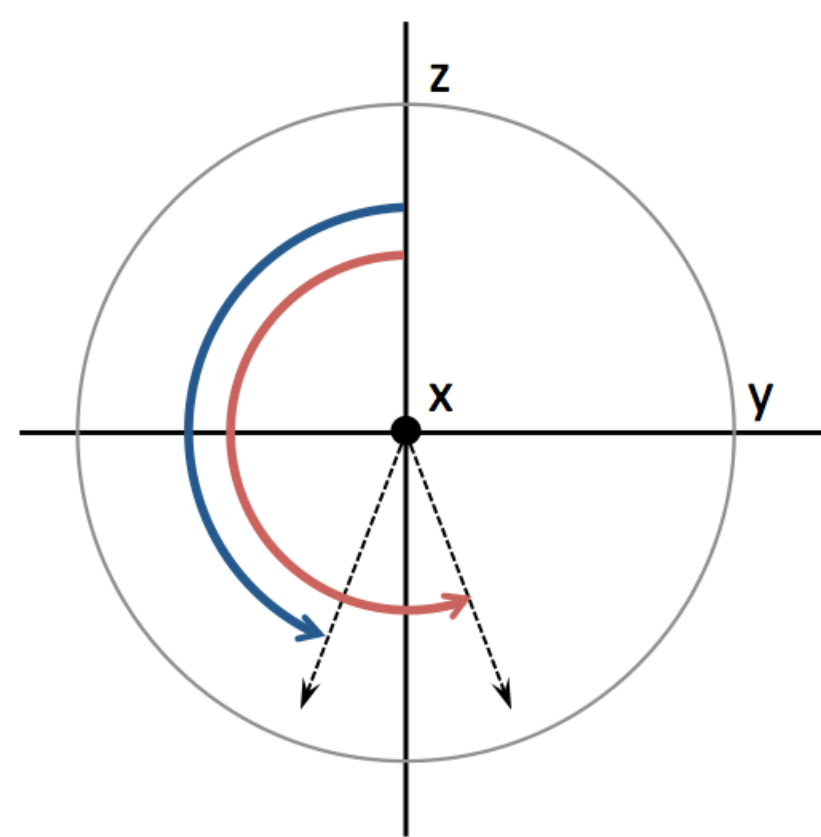


Composite Pulses

Composite pulses consist of contiguous pulses with different phase and duration. ^[1] They perform same action as standard pulse, but use phase of signal or the axis of rotation to compensate for errors such as B_1 inhomogeneity and frequency offset.

Higher amplitude B_1 over-rotates, lower amplitude under-rotates.

Broad bandwidth at W-band, requires **broad bandwidth pulses**

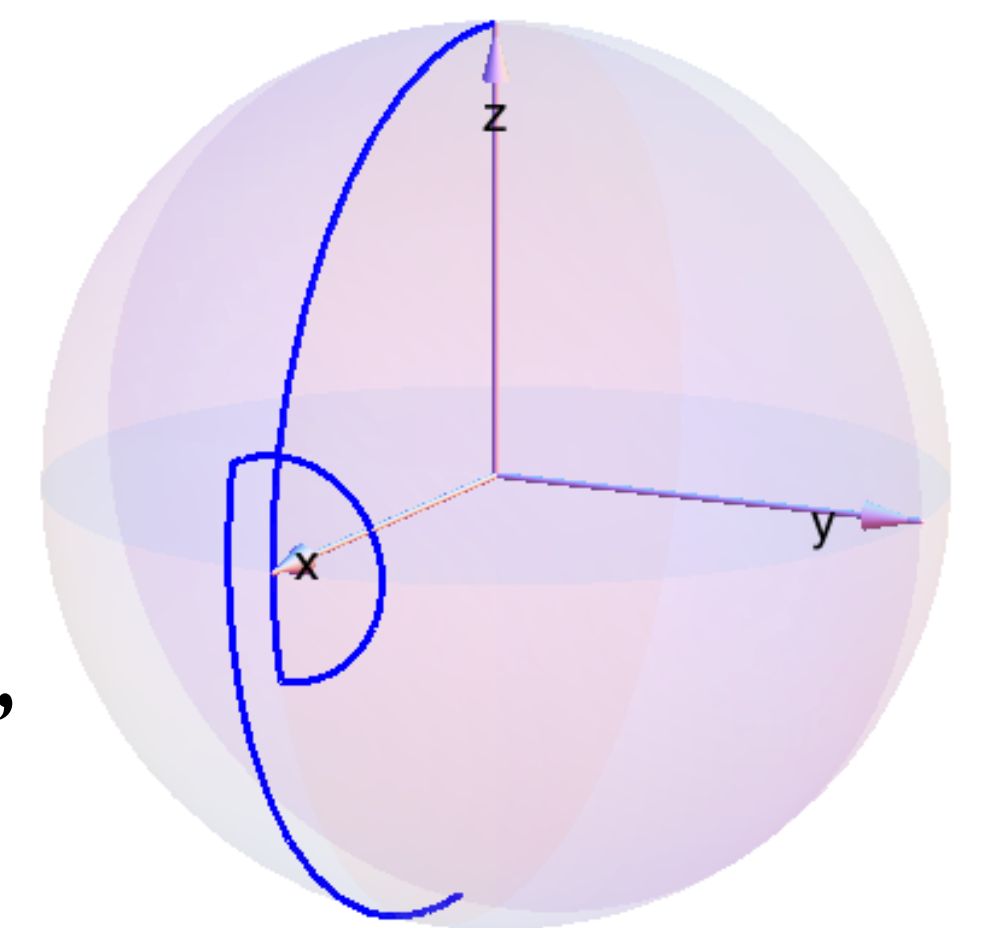


$90_{90}180_{90}90$ ^[1] sequence:

90° rotation around y
 180° rotation around x
 90° rotation around y } Overall π (inversion)

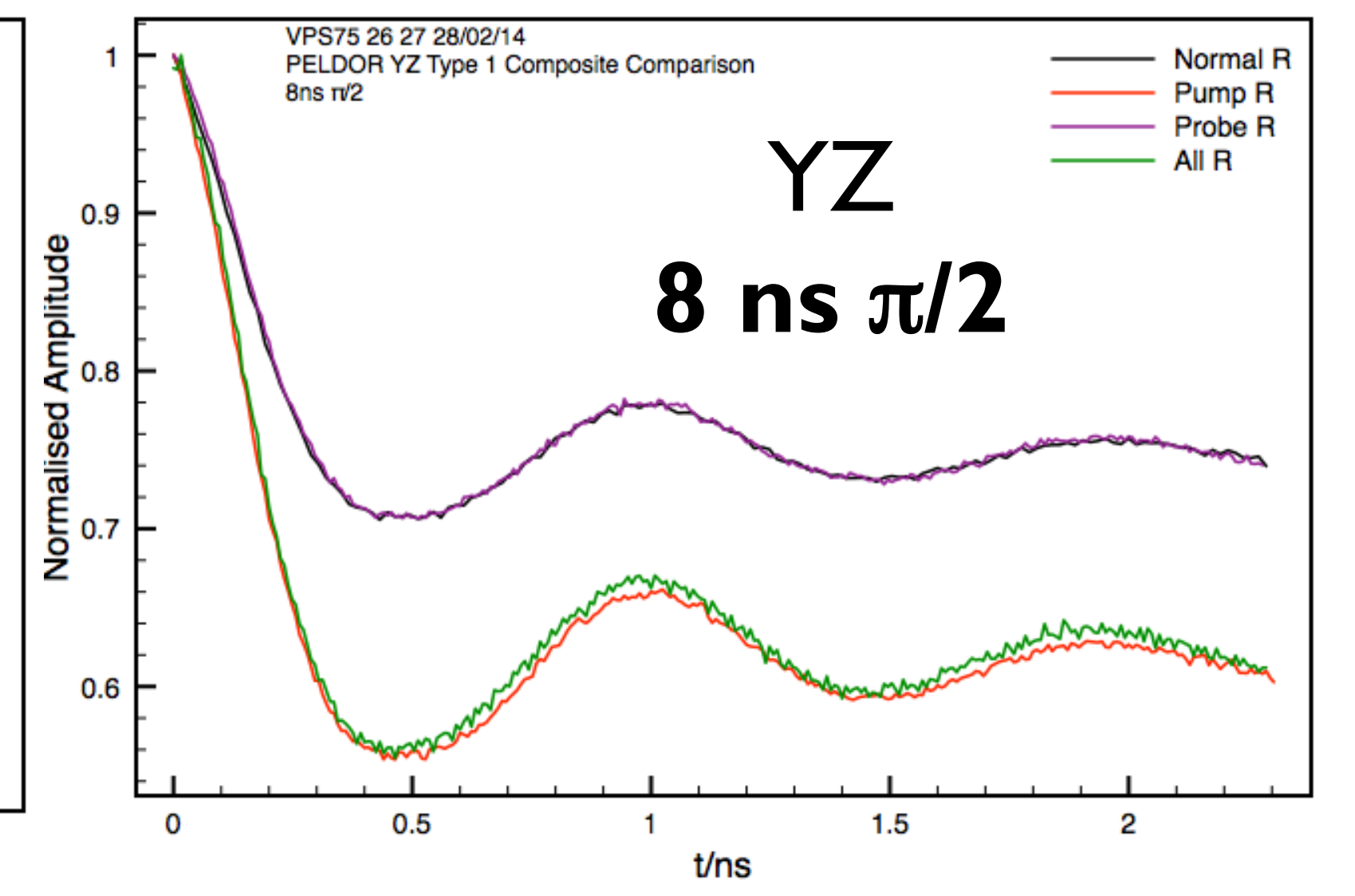
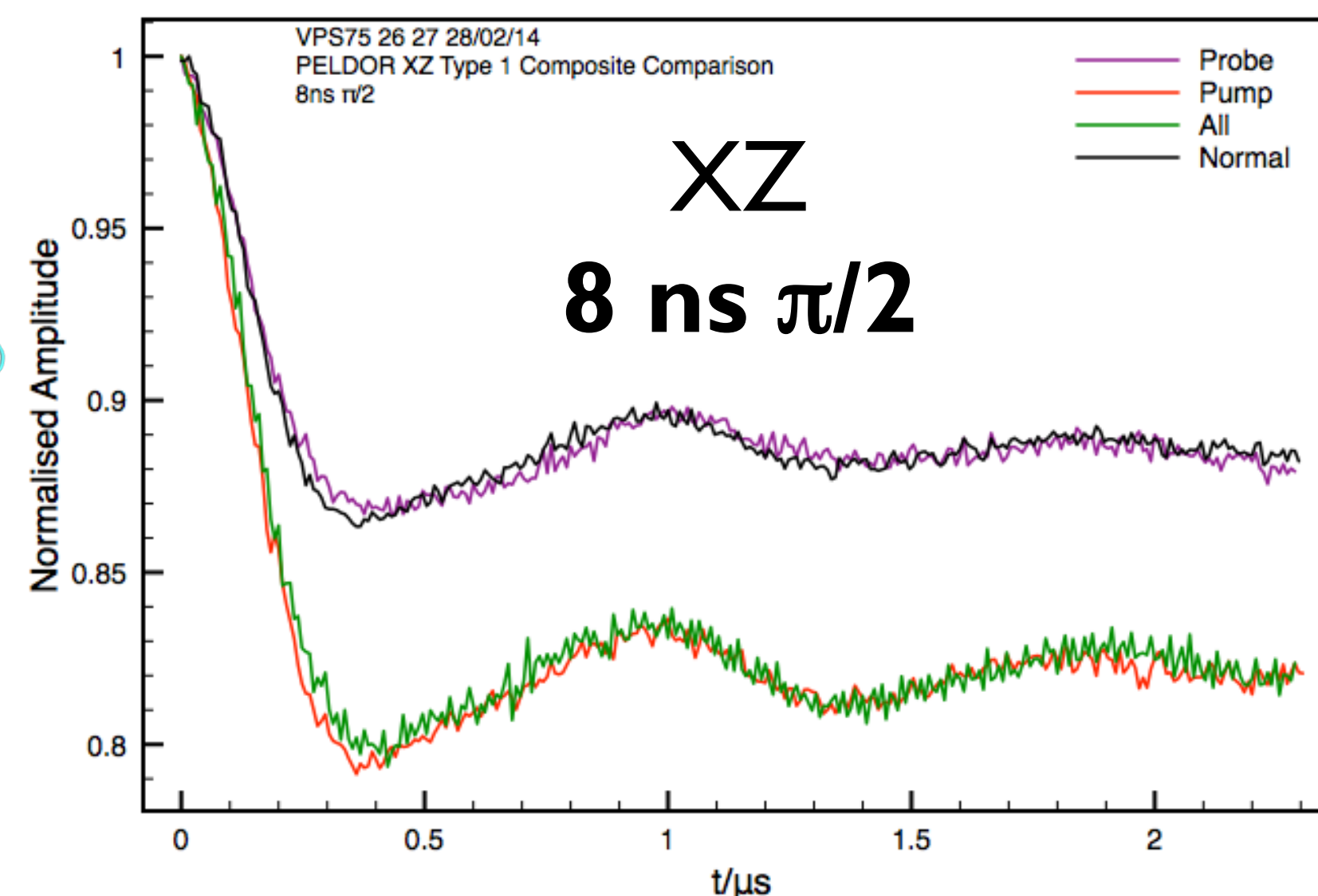
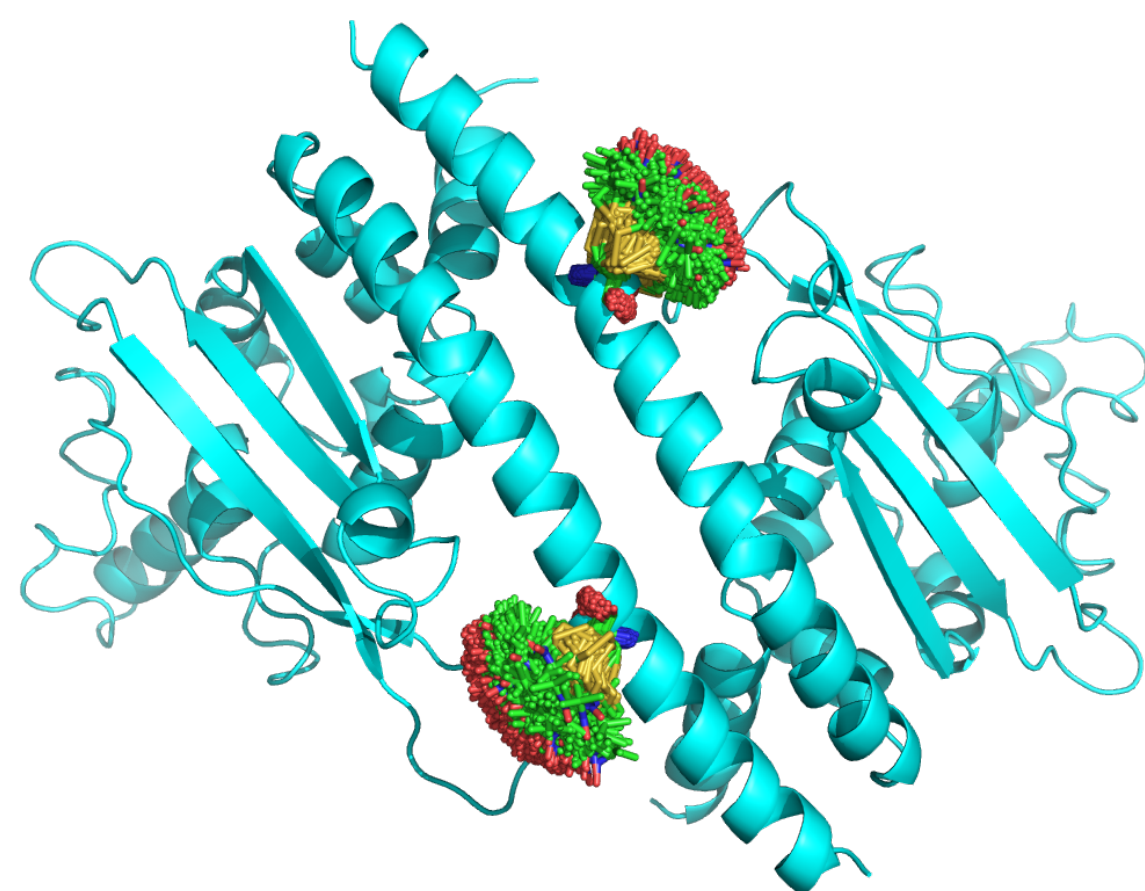
Over-shooting spins rotated back towards +z, undershooting spins helped towards -z.

=> **Larger population reaches target.**



Composite PELDOR

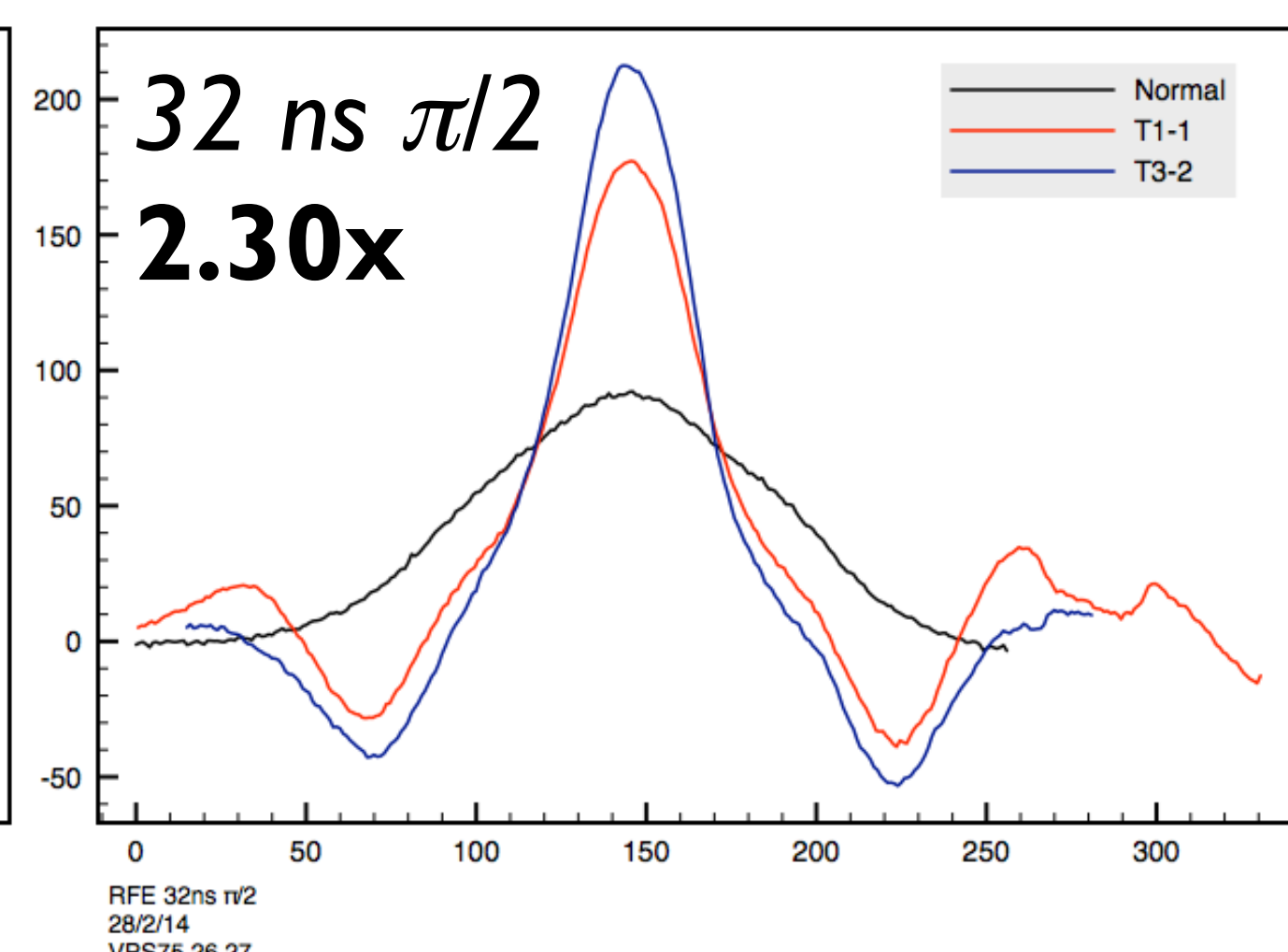
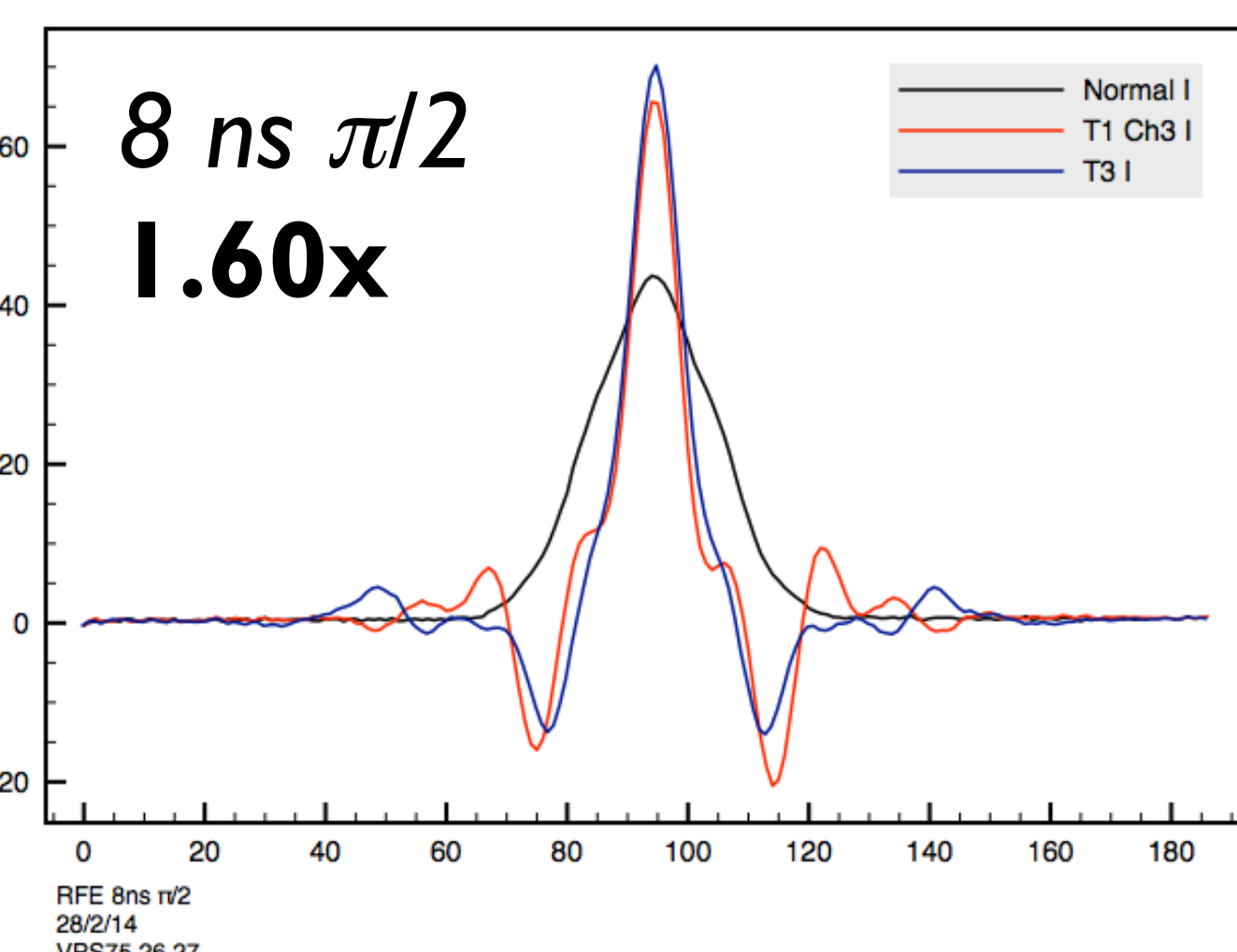
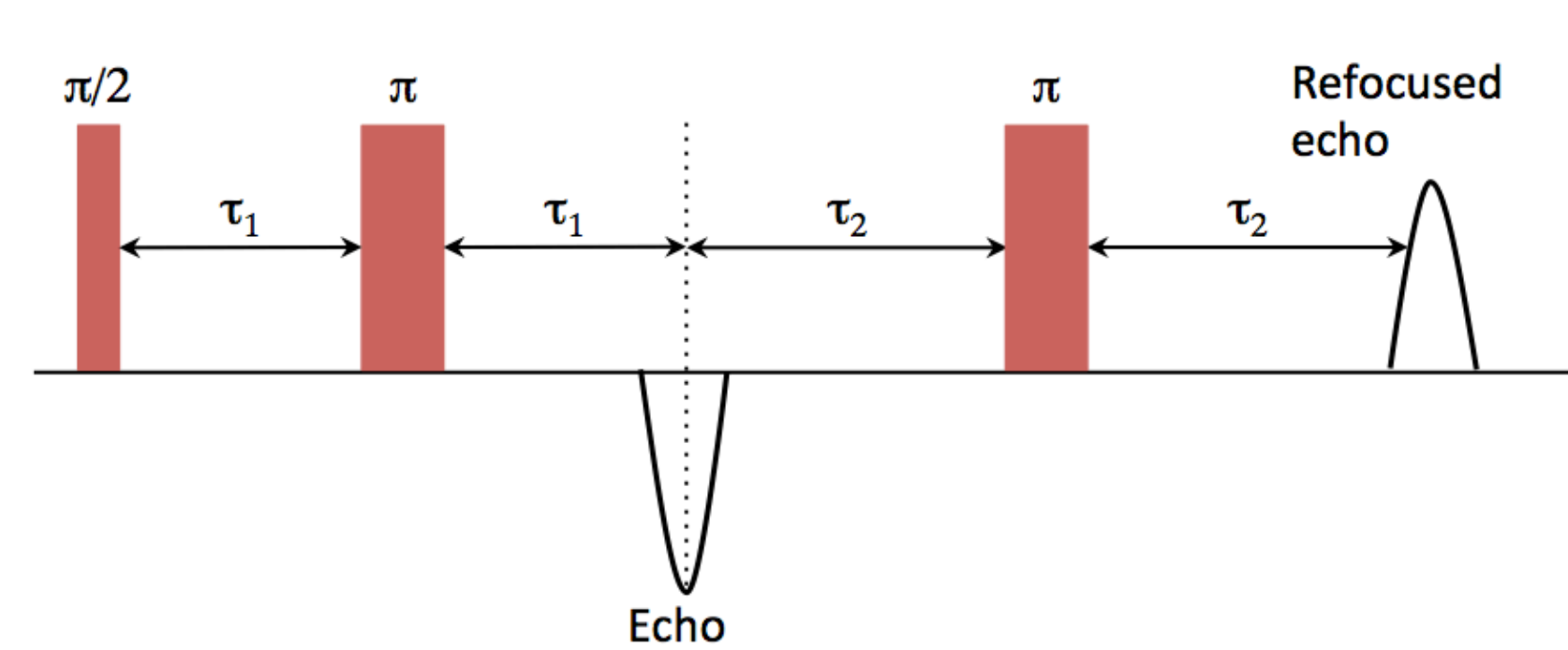
PELDOR carried out on Rx nitroxide labelled VPS75 26 27. π pulses replaced with composites. Pump and all composite show best improvement, up to 65% larger modulation depth.



Refocused Echo Enhancement

Significant enhancement from composite pulses. Echo amplitude increases for composite versus normal pulses.

Longer pulse lengths (lower bandwidth of excitation) show larger enhancement.

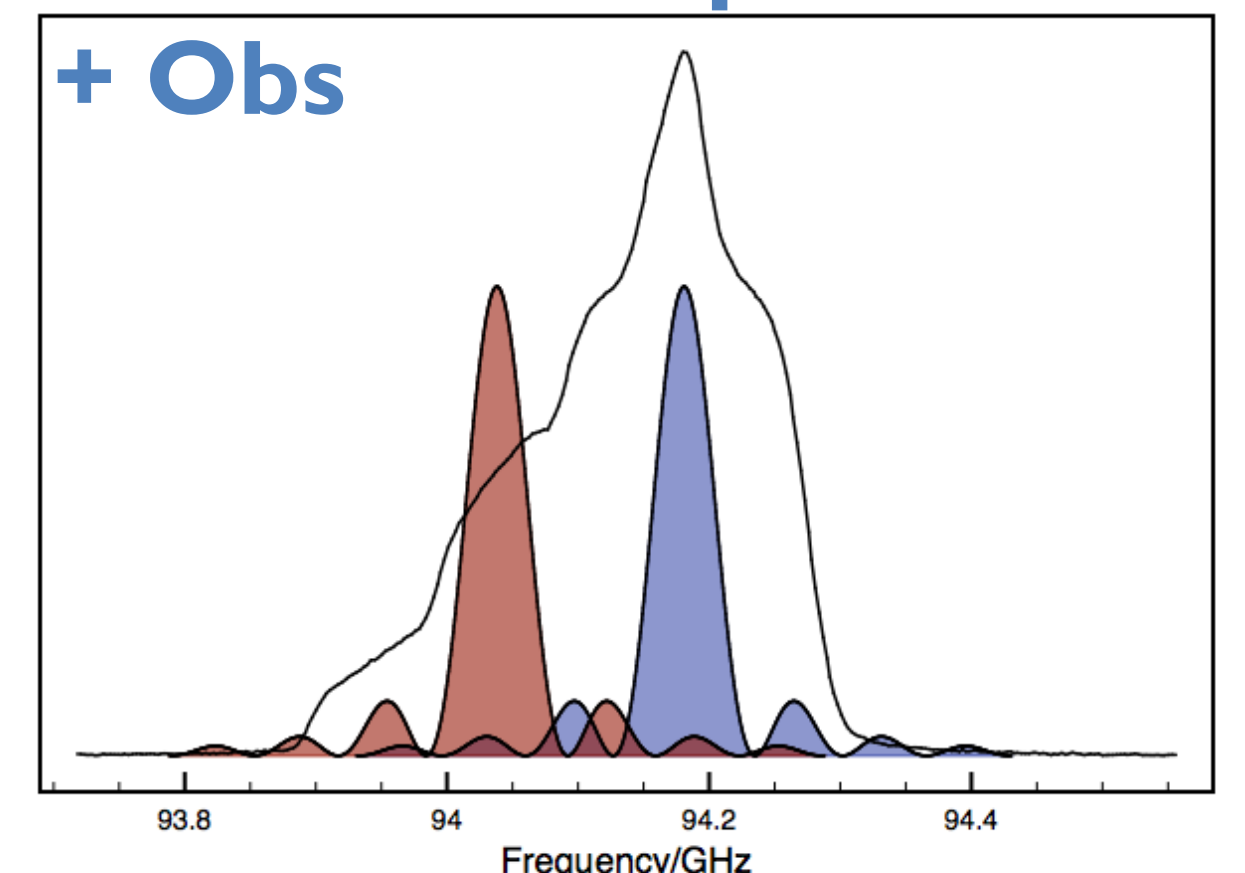


Excitation bandwidths and B_1 compensation

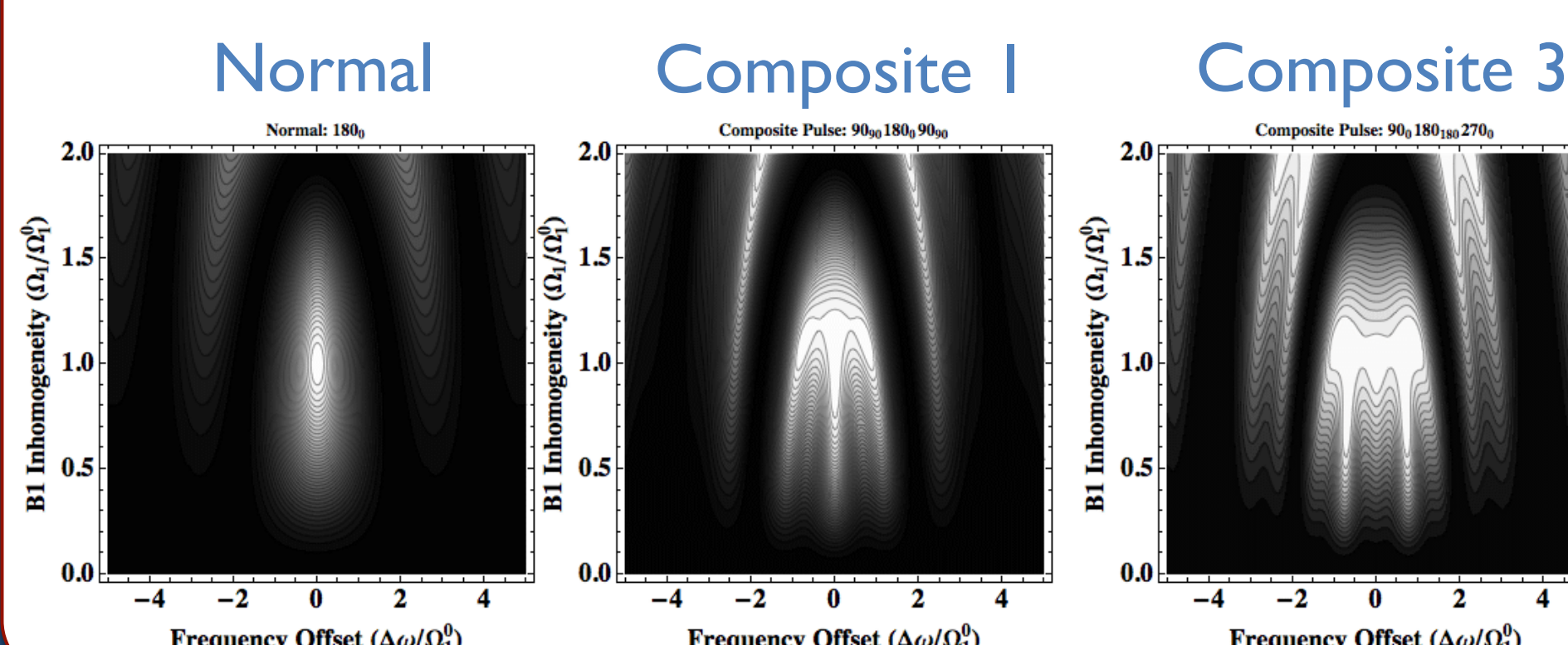
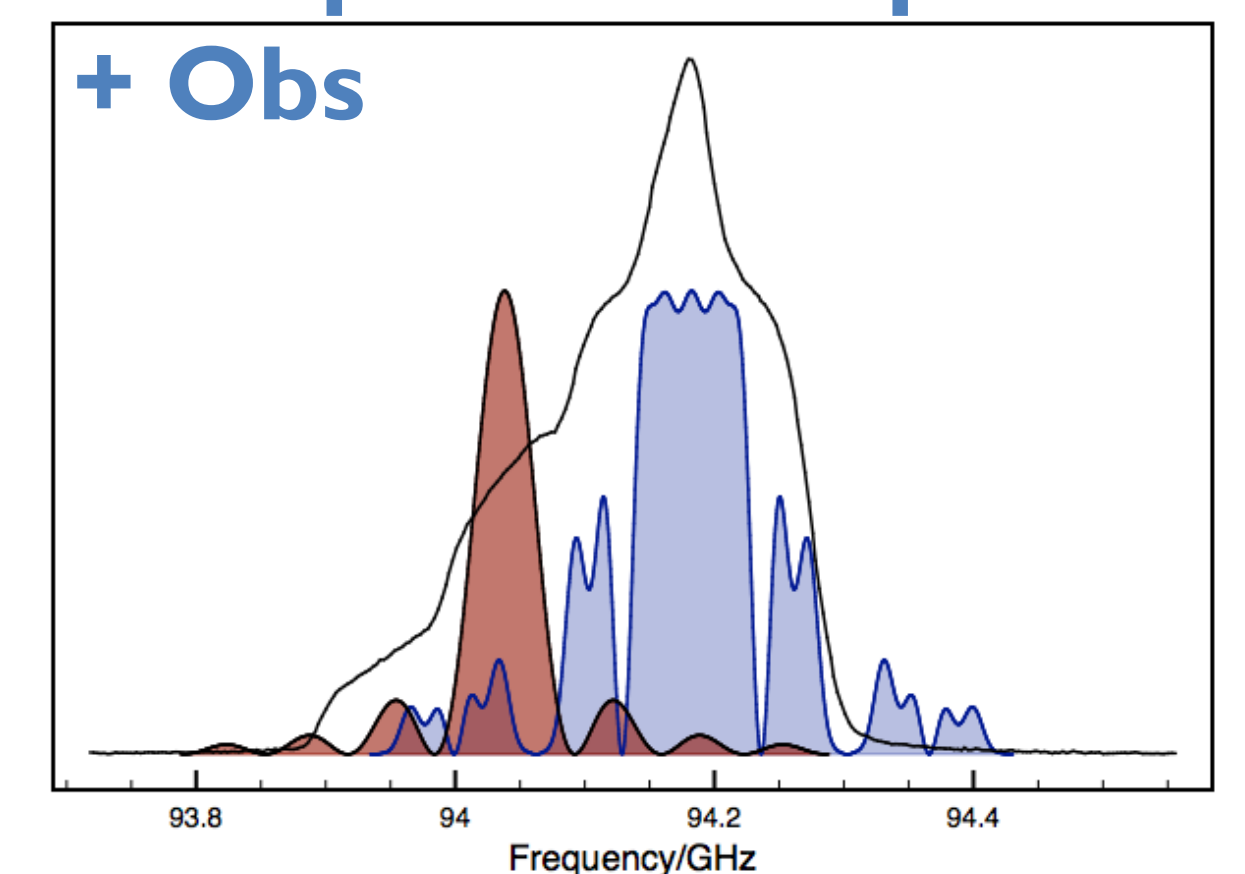
Excitation bandwidth of composite much broader than standard pulse, able to invert more of Y peak (pump) leading to deeper modulation.

Contours of B_1 versus Freq offset show much greater inversion (white areas) outside of optimal range.

Normal Pump + Obs



Composite Pump + Obs



References

- [1] M.H. Levitt, Composite Pulses, Encyclopedia of Nuclear Magnetic Resonance, Wiley (1996)
- [2] P.A.S. Cruickshank et al. Rev. Sci. Instrum. 80, 103102 (2009)