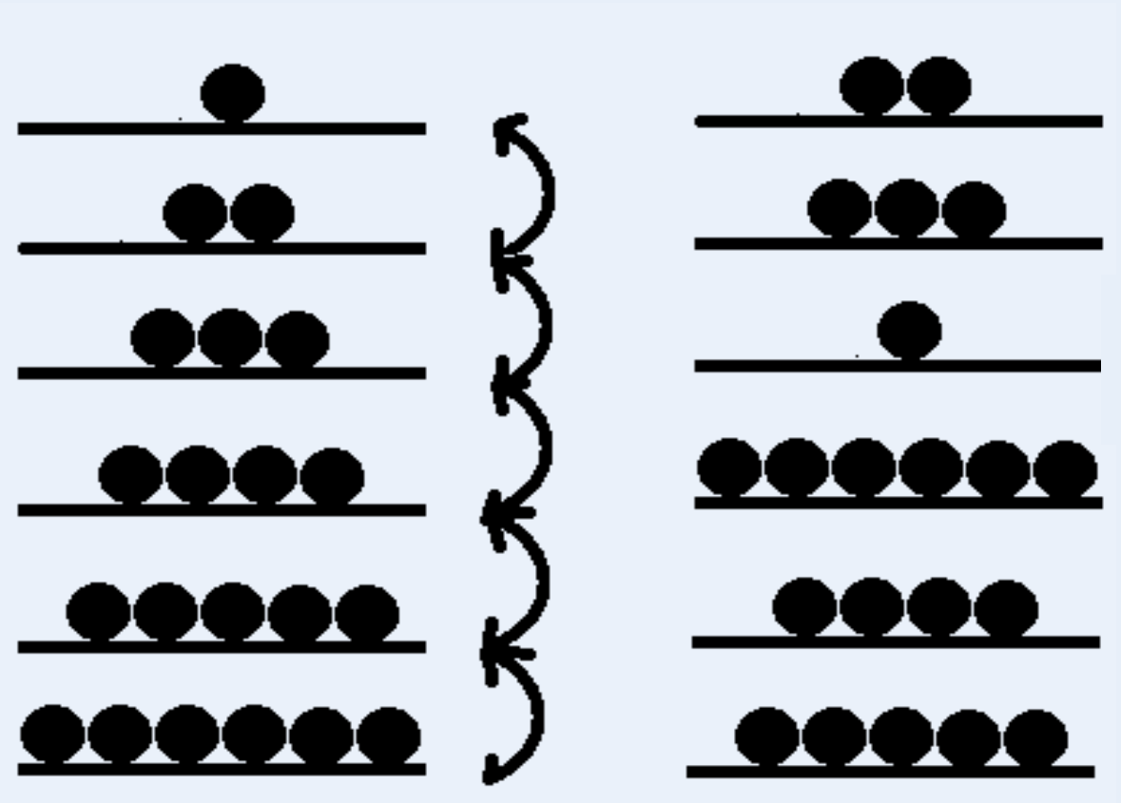
Pulse shapes for sensitivity enhancement in solid-state NMR of quadrupolar nuclides based on optimal control theory

Yijue Xu， Frédéric Perras and David L. Bryce

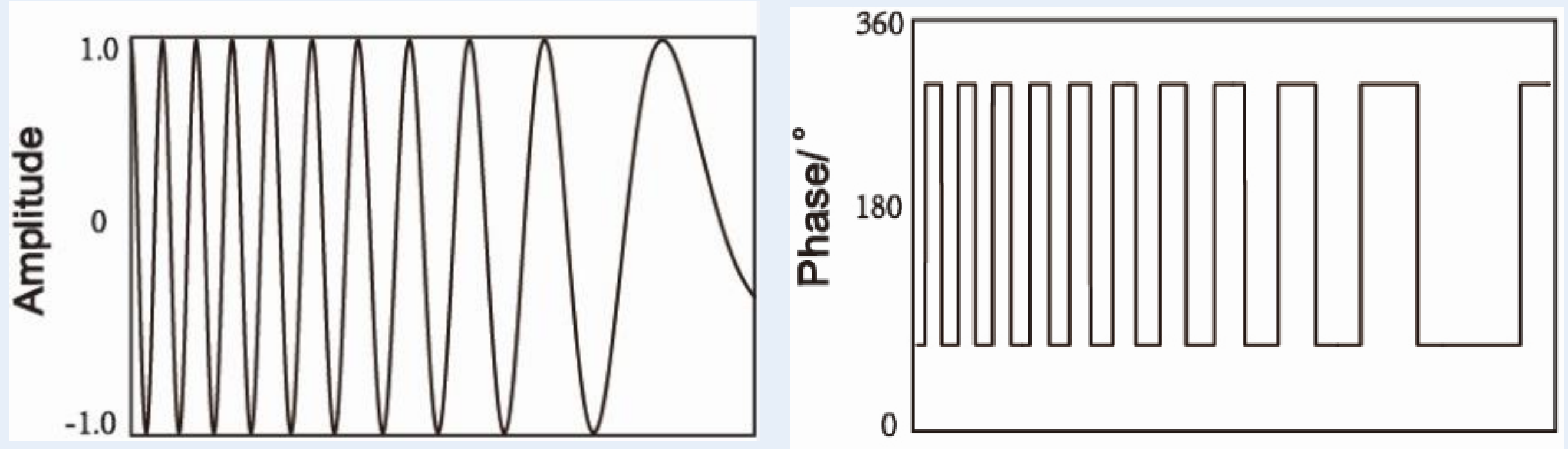
Introduction

Solid-state nuclear magnetic resonance (NMR) spectroscopy is an advanced analytical technique which allows for the study of quadrupolar nuclei; however, its most significant challenge is sensitivity. The objective of this research is to use optimal control theory to develop shaped NMR pulses for signal enhancement in solid-state NMR of quadrupolar nuclides.

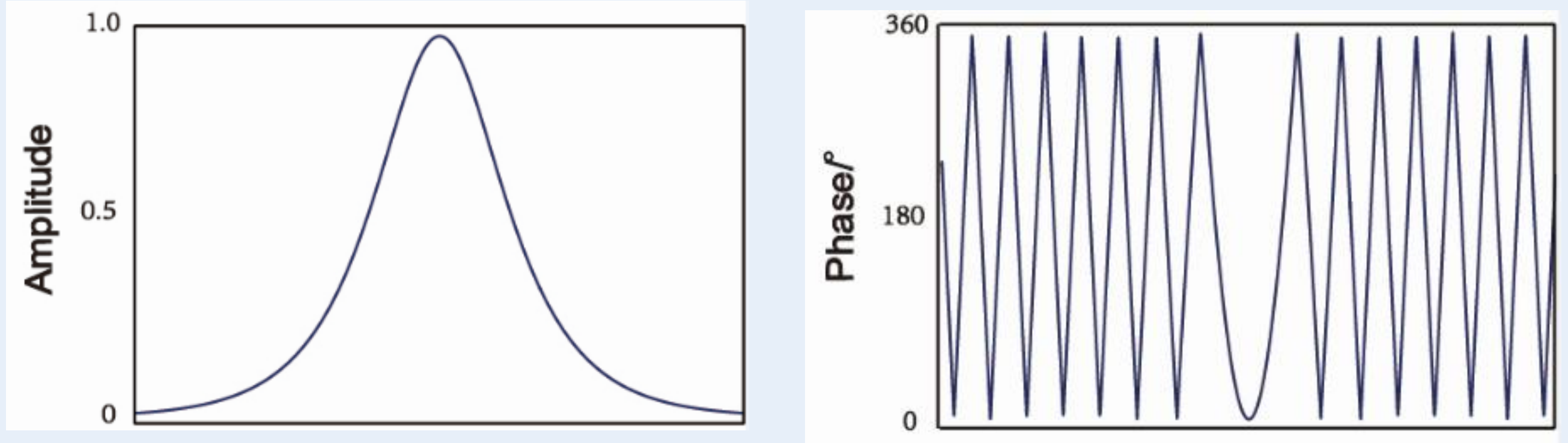
Enhancement is achieved by transferring the magnetization from satellite transitions (ST) to the central transition (CT). The larger the polarization of the latter we get, the better the enhancement that is achieved. If all outer STs are inverted before inversion of the inner STs, a maximum enhancement of 2I can be obtained[1]. I is the nuclear spin quantum number.



The first method to achieve ST inversion is via Double Frequency Sweeps (DFS).



The second way is via Hyperbolic Secant (HS) pulses[1].

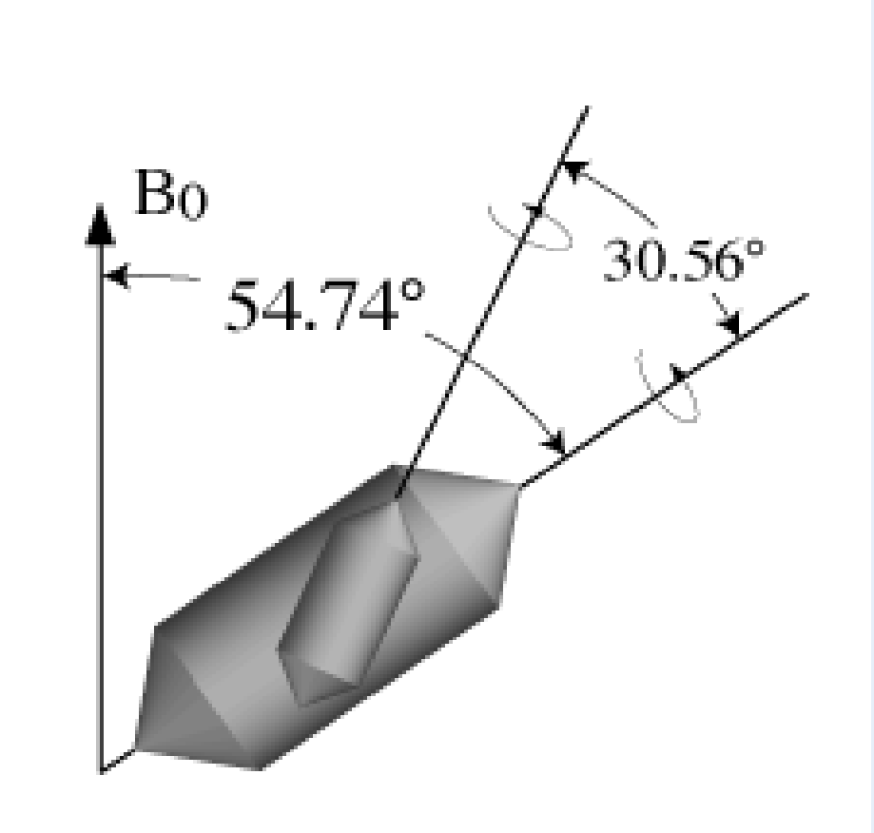


First two methods both perform frequency sweeps to adiabatically invert the satellite transitions.

The third way to achieve signal enhancement of the CT is to apply a COMPACT-n(Composite Pulses Adapted for Central Transitions) pulse, which has the form of $(\tau_p)_x(2\tau_p)_{-x}(3\tau_p)_x\ldots(n\tau_p)_{\pm x}$, where τ_p is the length of the first pulse, $4 \leq n \leq 7$, and the phase of the last pulse is +x or-x, for odd or even values of n, respectively. This method can provide a more efficient conversion of Zeeman population difference between the STs and the CT.[2]

For Optimal Control Theory (OCT), is a method to optimize complex pulse schemes. Using hundreds to thousands of pulses, it can efficiently optimize NMR experiments in terms of amplitudes, phases, offsets and so on.

Double Rotation (DOR) is a method that can narrow shape line to obtain higher resolution. There are two rotors, one inside the other. Spinning the sample in this way can average the anisotropic quadrupolar interaction so to give sharper lines and a better spectral resolution[3].



Theoretically, applying optimal control theory to a shaped pulse that is already known to provide signal enhancement can provide an even more effective and efficient enhancement[4].

Results

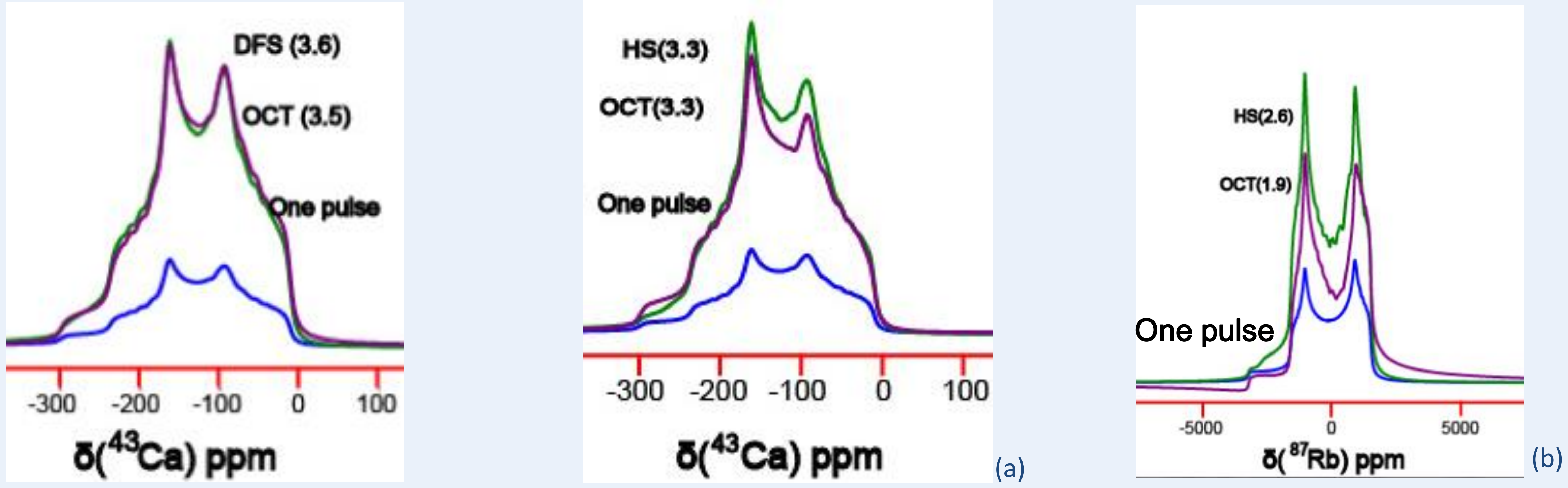


Figure 1. Comparison of the ^{43}Ca and ^{87}Rb NMR signal enhancement obtained with one pulse (blue), with HS or DFS (green) and after application of optimal control theory(purple). Simulations were performed in SIMPSON. In (a) the DFS pulses swept from 250kHz to 30kHz. In (b) the HS pulse had a 70kHz offset and a 5kHz sweep width. In (c) the HS pulse had a 70kHz offset and a 5kHz sweep width.

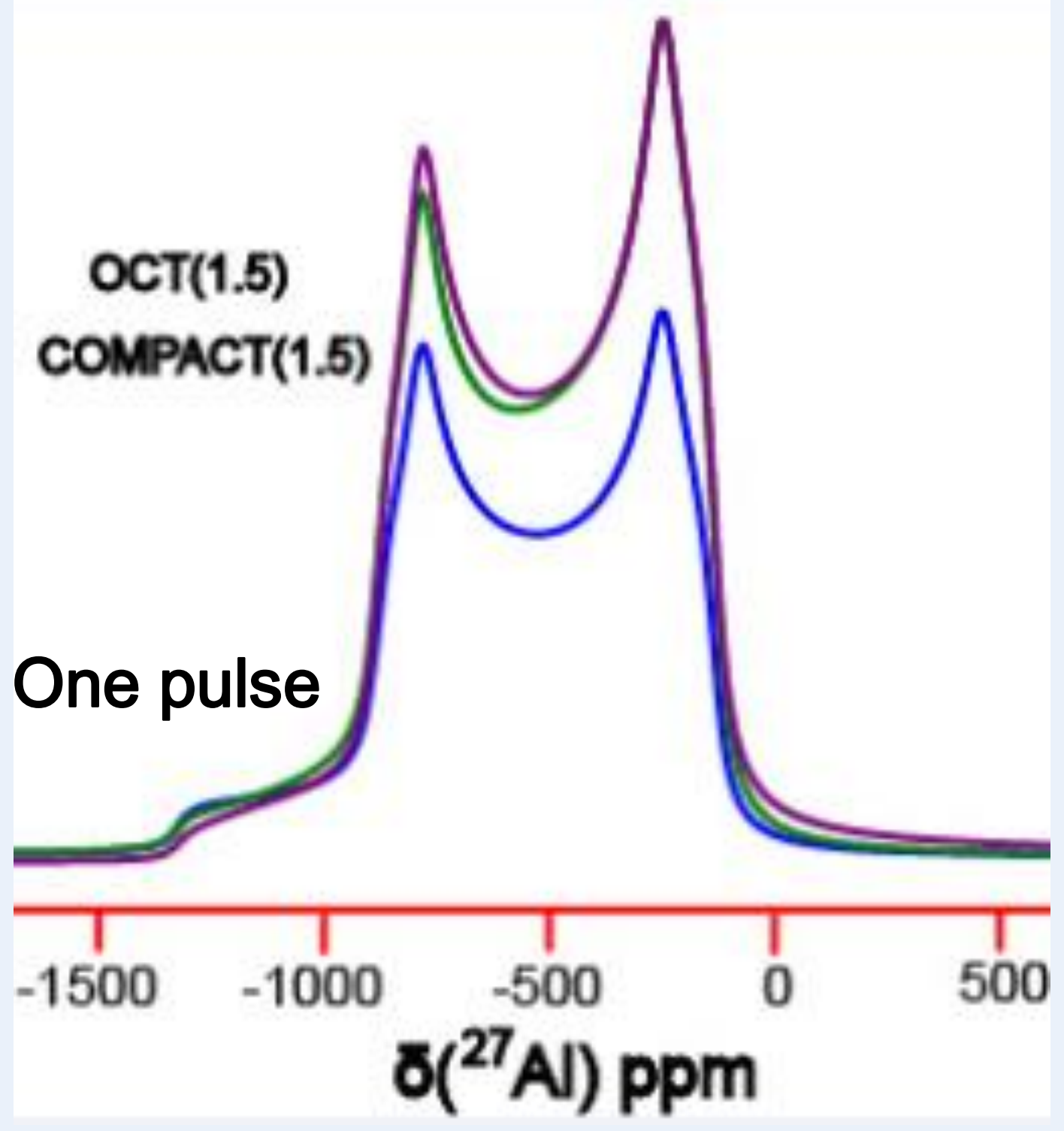


Figure 2. ^{27}Al signal enhancement demonstrated with a single pulse (blue), with COMPACT-7 (green) and after applying optimal control theory(purple) in SIMPSON. Fitting of the line shapes gave a quadrupolar coupling constant C_Q =2.39MHz, and the asymmetry parameter η=0.73

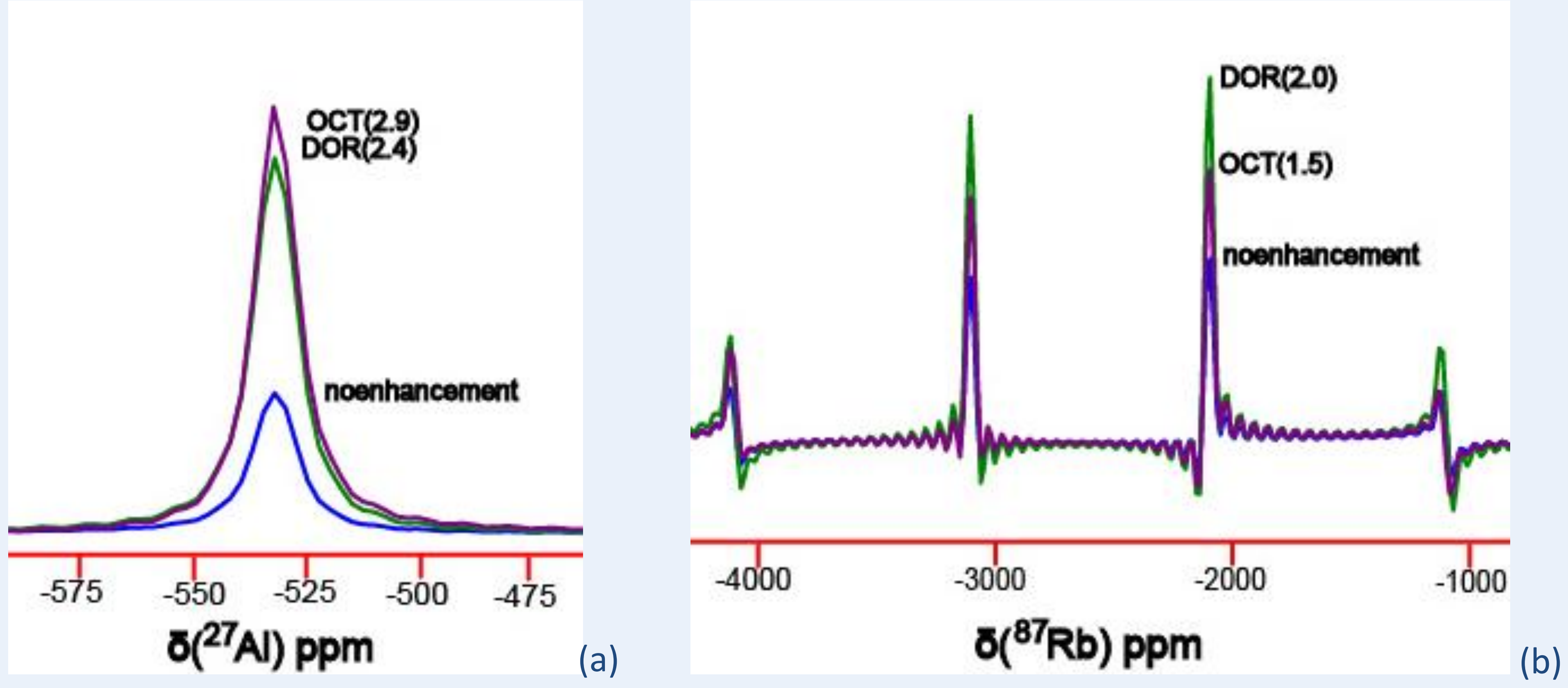


Figure 3. (a) ^{27}Al DOR signal enhancement (green) with the outer rotor spinning at 1 kHz and enhancement after applying optimal control theory (purple) in SIMPSON. (b) ^{87}Rb DOR signal enhancement (green) with the outer rotor spinning at 1 kHz and enhancement after applying optimal control theory (purple) in SIMPSON.

Methodology

- Hundreds of adjustments of parameters(start and end frequencies, maxrf for DFS pulses and offset and maxrf for HS pulses) were done in EXCEL to optimize the HS and DFS shapes. Used the SIMPSON simulation software to test suitability of existing shaped pulses under MAS and DOR condition.
- Used DFS and HS pulses as a starting point and applied optimal control theory to design more effective pulse shapes under MAS and DOR condition.
- Adjusted n value from 4 to 7 in COMPACT-n pulse to optimize the pulse shape. COMPACT-7 sequence was carried out with the SIMPSON.
- Used COMPACT-7 sequence as a start point and applied optimal control theory.

Conclusion

- The enhancement based on optimal control theory was significant for the ^{27}Al DOR signal. However, in the case of the hyperbolic secant, the signal improvement decreased after the application of optimal control theory.
- Investigating the reasons behind the OCT'S failure in some aspects of this project will likely reveal significant insight.
- The promising results obtained for DOR NMR spectroscopy are currently being investigated experimentally in our lab

References

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