Engineering Spin Hamiltonians Using Multiple Pulse Sequences in Solid-State NMR

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Introduction

Multiple pulse sequences are often used to manipulate spin Hamiltonians in solid-state NMR. The average Hamiltonian theory (AHT) developed by Haeberlen and Waugh [1] is a proven powerful theoretical framework for analyzing multiple-pulse sequences in solid-state NMR. Designing valid multiple pulse sequences has continued to be an important topic, and many relevant methods based on symmetry have been proposed. A fundamental issue in designing multiple pulse sequences in the spin space is to select a specific spin Hamiltonian of interest, while suppressing any other Hamiltonians. This would allow us to simplify the spin system in order to obtain useful spectroscopic information. Here, we use AHT to expand the spin Hamiltonians into a set of average sub-Hamiltonians that are multiplied by different factors determined only by flip-angles and phases of the applied pulses in the multiple pulse sequences. To select any desired sub-Hamiltonian, we turn this set of factors into constraint equations and by solving such equations we can select this given sub-Hamiltonian while suppressing any other sub-Hamiltonians. This new procedure allows us to design a new homonuclear decoupling scheme [2].

Experimental

All NMR experiments were carried out on a Bruker Avance 600 MHz NMR spectrometer using a home-built low-E ^{1}H-^{15}N double-resonance static NMR probe with a rectangular coil. A ^{15}N-acetyl-valine crystal sample has been used to demonstrate the performance of the new decoupling sequence.
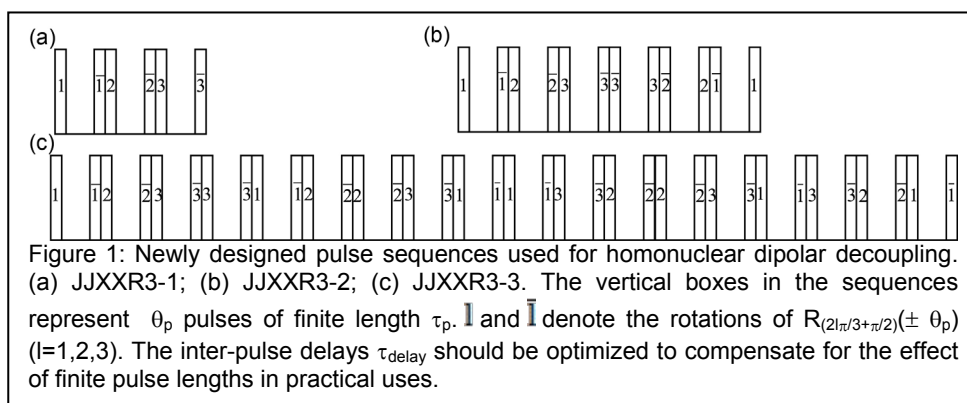

Figure 1: Newly designed pulse sequences used for homonuclear dipolar decoupling. (a) JJXXR3-1; (b) JJXXR3-2; (c) JJXXR3-3. The vertical boxes in the sequences represent θ_p pulses of finite length τ_p. $\mathbf{1}$ and $\bar{\mathbf{1}}$ denote the rotations of $R_{(2I\pi/3+\pi/2)}(\pm\ \theta_p)$ (I=1,2,3). The inter-pulse delays τ_{delay} should be optimized to compensate for the effect of finite pulse lengths in practical uses.

Results and Discussion

Figure 1 shows the newly designed homonuclear decoupling sequence in static solids. It has been confirmed in theory and in experiments that this decoupling scheme, in the presence of finite pulse length, effectively suppresses ^{1}H-^{1}H homonuclear dipolar interactions while establishing variable scaling factors on ^{1}H-^{15}N heteronuclear dipolar interactions and ^{1}H chemical shift interactions, depending on the flip-angle θ_p. As shown in Figure 2, when θ_p is close to 54.7°, this sequence possesses a large scaling factor with relatively low average decoupling field. When θ_p becomes ~120°, the scaling factor is almost zero. Further experiments utilizing this feature have been under consideration.
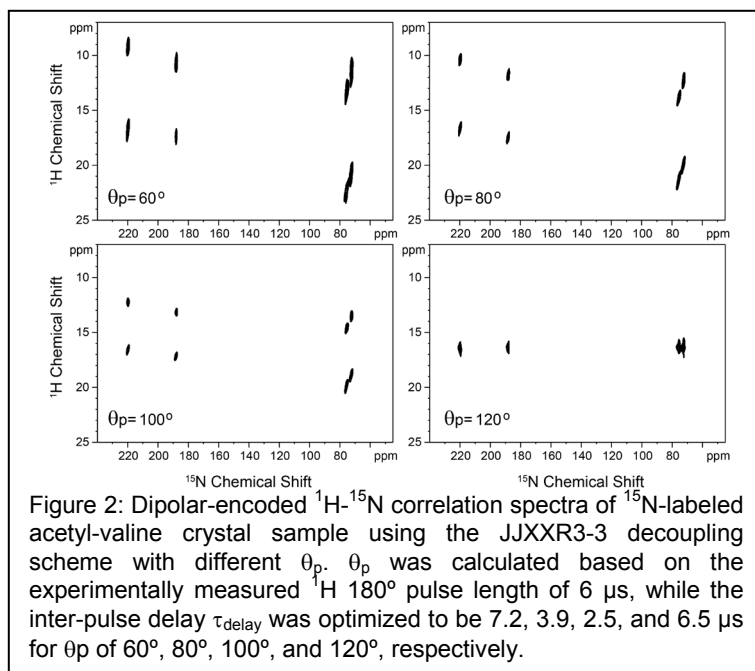
Acknowledgements

Figure 2: Dipolar-encoded ^{1}H-^{15}N correlation spectra of ^{15}N-labeled acetyl-valine crystal sample using the JJXXR3-3 decoupling scheme with different θ_p. θ_p was calculated based on the experimentally measured ^{1}H 180° pulse length of 6 μs, while the inter-pulse delay τ_{delay} was optimized to be 7.2, 3.9, 2.5, and 6.5 μs for θ_p of 60°, 80°, 100°, and 120°, respectively.

References

[1] Haeberlen, U., *et al.*, Phys. Rev., **175**, 354-467 (1968).
[2] Cui, J.Y., *et. al.*, J. Magn. Reson., **294**, 83-92 (2018).