Reduction of Proton-Driven Spin Diffusion Artifacts from 2D zfr-INADEQUATE MAS NMR Spectra

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Introduction -
A significant shortcoming of the z-filtered refocused (zfr) INADEQUATE magic-angle spinning (MAS) nuclear magnetic resonance (NMR) pulse sequence is the possibility of artifacts introduced during the z-filter due to proton-driven spin diffusion (PDSD) whereby extra peaks in the single-quantum dimension (from other sites in the molecule) appear correlated (incorrectly) with a given double-quantum frequency. This is a problem when the spinning speeds are too slow (less than 15 kHz) to sufficiently average the proton-proton homonuclear dipolar couplings. This would be especially important when working with large volume rotors (where top speeds are often 5 to 8 kHz) that are difficult to spin fast enough to completely average the homonuclear couplings. In our experiments we used the frequency-switched Lee-Goldberg (FSLG) method of homonuclear decoupling during the z-filter to remove the artifact peaks. This method has the advantage of being quite easy to setup and implement on a modern NMR spectrometer.

FSLG Implementation -
The FSLG decoupling is accomplished by applying the \( ^1H \) decoupling field offset from the \( ^1H \) resonant frequency such that the effective RF field direction lies at the magic-angle (54.74°) with respect to the large magnetic field (\( B_0 \)) axis. This is the spin equivalent of magic-angle spinning and will hence remove all dipolar couplings but leave behind any scalar (J) couplings. These scalar couplings serve to help dephase the unwanted zero-quantum coherences during a z-filter. Below are spectra of adamantane taken with normal on-resonance decoupling (left) and appropriately optimized FSLG decoupling on the right. Notice that the 130 Hz H-C scalar coupling is reduced to 65 Hz (0.500 scaling factor) by the FSLG sequence. This is very close to the 0.577 ratio expected for an optimized FSLG decoupling sequence. In both cases all heteronuclear dipolar coupling is removed.

PQSD -
The zfr-INADEQUATE spectra for isoleucine were acquired with differing z-filter times without FSLG. These ranged from 1 ms (top right) to 250 ms (bottom right). What is clear in these spectra is the increased number of artifact peaks as the z-filter time is made longer. A similar study has been done for variable spinning speed with a similar outcome (faster speed produces fewer artifacts). The source of these extra peaks is the transfer of magnetization (coherent signal) between carbon sites during the z-filter which is mediated by the homonuclear H-H dipolar couplings (PQSD). These can be eliminated by either fast spinning or short z-filter times. These solutions are not always possible for all setups which led us to pursue the FSLG experiment.

Conclusions -
The simple addition of FSLG homonuclear decoupling to the z-filter in the experiment, we were able to effectively suppress artifact peaks. The left spectra show the zfr-INADEQUATE taken with (below) and without (above) FSLG decoupling. The relative signal-to-noise in the top spectrum is much lower than the bottom, primarily as a result of retention of full intensity in the non-artifact peaks. The spectra to the right are slices through specific peaks in the double-quantum dimension and illustrate the relative size of the artifact peaks (indicated by arrows) in the various slices.