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Reduction of spin diffusion artifacts from 2D zfr-INADEQUATE MAS NMR spectra

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ABSTRACT

The primary shortcoming of the z-filtered refocused INADEQUATE MAS NMR pulse sequence is the possibility of artifacts introduced during the z-filter due to spin diffusion where by extra peaks in the single-quantum dimension (from other sites in the molecule) appear correlated 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 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 most modern NMR spectrometers.

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1. Introduction

Magic-angle spinning combined with RF irradiation has proven to be an extremely important tool for the study of solid samples with nuclear magnetic resonance [1–12]. Increasing the number and diversity of experiments that work well under MAS conditions has been a continued goal of many researchers over the last 20 years. The INADEQUATE experiment [13] is well known in the liquid state NMR community as a method that gives unambiguous through-bond homonuclear chemical connectivities using scalar (*J*) couplings, though it is inherently insensitive and often requires full or partially labeled samples. Given the anti-phase nature of this experiment and the difficulty of applying this to solid samples, modifications have been made over the years, ultimately leading to the refocused INADEQUATE for solid-state NMR [14]. Certainly other experiments have been suggested [15–23] that have both advantages and disadvantages, but the INADEQUATE has proven very versatile and worth further examination.

In the paper published by Cadars et al., the z-filtered refocused (zfr)-INADEQUATE MAS NMR experiment was described and discussed [24]. The authors showed that using a z-filter of 1–5 ms could significantly improve the quality of the lineshape of the peaks found in the spectra. In particular the z-filter removed all of the ^{13}C zero-quantum coherences not stored as z-magnetization during the filter. The major drawback of this approach is the unwanted transfer of magnetization between ^{13}C atoms during the z-filter period produced by spin diffusion. It was suggested in the Cadars paper that some heteronuclear dipolar interactions actually need to be present to help eliminate the undesired zero-quantum coherences; however, when spin diffusion is too large, the resulting spectrum may contain artifact peaks. The simple solution is to spin the rotor fast enough that the ^{1}H–^{1}H homonuclear dipolar couplings are eliminated (or at least significantly reduced). This approach then relies purely on the dephasing due to evolution of the zero-quantum flip-flop signal components due to homonuclear ^{13}C–^{13}C *J*-coupling. These couplings are weak and the z-filter period then must be sufficiently long for these coherences to dephase completely and render the final spectrum artifact free. In practice there will always be some residual ^{13}C–^{1}H dipolar coupling which will also serve to dephase these zero-quantum coherences. The original zfr-INADEQUATE works well for the high speed small rotors, but when larger sample volume is important (5 mm and larger rotors), it can be impossible to spin fast enough for the couplings to be sufficiently averaged. In this paper we suggest that reducing (through RF pulse averaging techniques) the homonuclear ^{1}H–^{1}H couplings, but leaving the ^{1}H–^{13}C couplings in place can help to eliminate the unwanted signal from spin diffusion during the z-filter in this experiment. In the past, many approaches have been used to eliminate (or reduce) the ^{1}H–^{1}H homonuclear couplings using spin space averaging (via pulses) rather than spatial (via sample rotation) averaging; these include WAHUHA [25], FSLG [26,27], PMLG [28], DUMBO [29–32] and others [33]. For our experiments we chose to use the FSLG because it is one of the most robust windowless homonuclear decoupling schemes available when detection is not required during the decoupling. The DUMBO sequences introduced by the Emsley group would potentially improve overall

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homonuclear decoupling efficiency, but the difficulty in implementation may outweigh the advantages for most spectrometers. In the case of reducing the spin diffusion during the z-filter, the homonuclear decoupling does not have the same effectiveness requirements you might find in a ^{1}H indirect or direct observe experiment.

1.1. Pulse sequence

The pulse sequence used for the zfr-INADEQUATE experiments was identical to that used in previous work [24]. The only modification was the addition of FSLG [26] decoupling during the z-filter as seen in Fig. 1. The FSLG technique works by continuously rotating the proton magnetization about an effective RF field pointed along the magic-angle with respect to the large static magnetic field. This serves to average the homonuclear dipolar and *J*-couplings while leaving heteronuclear dipolar and *J*-couplings unaffected other than a scaling factor. By alternating the RF irradiation frequency between the two Lee–Goldberg conditions the pulse errors are partially compensated. The pulse phases were cycled to select the coherence path shown in Fig. 1, then acquired using the method of States [34] to achieve phase sensitivity in both dimensions, including the pulses to select only the zero-quantum coherences ($\mathbf{I}_{z,A}$, $\mathbf{I}_{z,B}$, $\mathbf{I}_{+,A}\mathbf{I}_{-,B}$, $\mathbf{I}_{-,A}\mathbf{I}_{+,B}$,$\mathbf{I}_{+,A}\mathbf{I}_{-,B}$, $\mathbf{I}_{-,A}\mathbf{I}_{+,B}$, etc.) during the z-filter. Zero-quantum coherences of the flip-flop type ($\mathbf{I}_{+,A}\mathbf{I}_{-,B}$, $\mathbf{I}_{-,A}\mathbf{I}_{+,B}$, etc.) were then dephased by the homonuclear *J*-coupling as well as the residual chemical shift anisotropy and heteronuclear dipolar couplings during the z-filter period. Because the proton chemical shift, as well as scalar and dipolar coupling evolution, were not of interest and did not directly affect our desired zero quantum ^{13}C coherences ($\mathbf{I}_{z,A}$, $\mathbf{I}_{z,B}$, etc.), the FSLG decoupling window did not require any bracketing magic-angle pulses, nor any absolute knowledge of the initial phase of the ^{1}H magnetization during the z-filter.

2. Experimental

All experiments were performed on a JEOL ECX-300 NMR spectrometer with ^{1}H and ^{13}C frequencies of 300.53 and 75.57 MHz using a Varian (Jakobsen-style) 5 mm double resonance MAS probe. For setup of the FSLG sequences, a sample of adamantane from Sigma–Aldrich was used with no further purification. To determine power levels and offset values for the FSLG sequence, CPMAS spectra of adamantane were taken with FSLG decoupling. By optimization of the parameters, we maximized the observed ^{1}H–^{13}C one-bond *J*-coupling splittings in these spectra (reaching values of approximately 70–80 Hz), getting very close to the theoretical maximum of $1/\sqrt{3} = 0.5773$ times the liquid ^{1}H–^{13}C *J*-coupling (121 and 136 respectively for the CH and CH$_2$ sites). The literature has multiple examples of how to improve the tuning of a FSLG experiment that the reader may also follow [35]. Using these parameters the INADEQUATE spectra were then acquired. The sample used for the INADEQUATE experiments was uniformly ^{13}C labeled isoleucine purchased from Cambridge Isotopes Laboratory and was also used without further purification. For our FSLG modified zfr-INADEQUATE, the sample of isoleucine was spun at 10 kHz. The proton 90° pulse was 2.5 μs; ramped cross-polarization using a contact time of 1.5 ms was used to transfer the magnetization between ^{1}H and ^{13}C atoms. We used SPINAL-64 proton decoupling during the evolution and acquisition periods at an RF field of 90 kHz. For the FSLG period, an offset of 66.7 kHz was used with an RF field of 94 kHz to produce an effective RF field aligned along the magic angle (54.74°). The ^{13}C pulses were 4.4 and 8.8 μs respectively for 90° and 180° pulses. For the variable z-filter experiments, the τ delay was set to 4.1 ms with a z-filter length of 1.5 ms, 6.4 ms or 25.6 ms. For the FSLG experiments the τ delay used to generate the double quantum coherences was set to 3.5 ms and the z-filter was set to 4.5 ms with the FSLG frequency changing every 9 μs. Quadrature detection in t_1 was achieved using States method using 45° phase shifts for the double quantum dimension with 64 scans (32 cosine and 32 sine) being added for each of the 64 t_1 increments. The total t_1 and t_2 acquisition times were 2.25 ms and 21.62 ms respectively. For the comparison to the normal z-filtered experiment, all parameters were kept the same except the FSLG pulses were turned off during the z-filter.

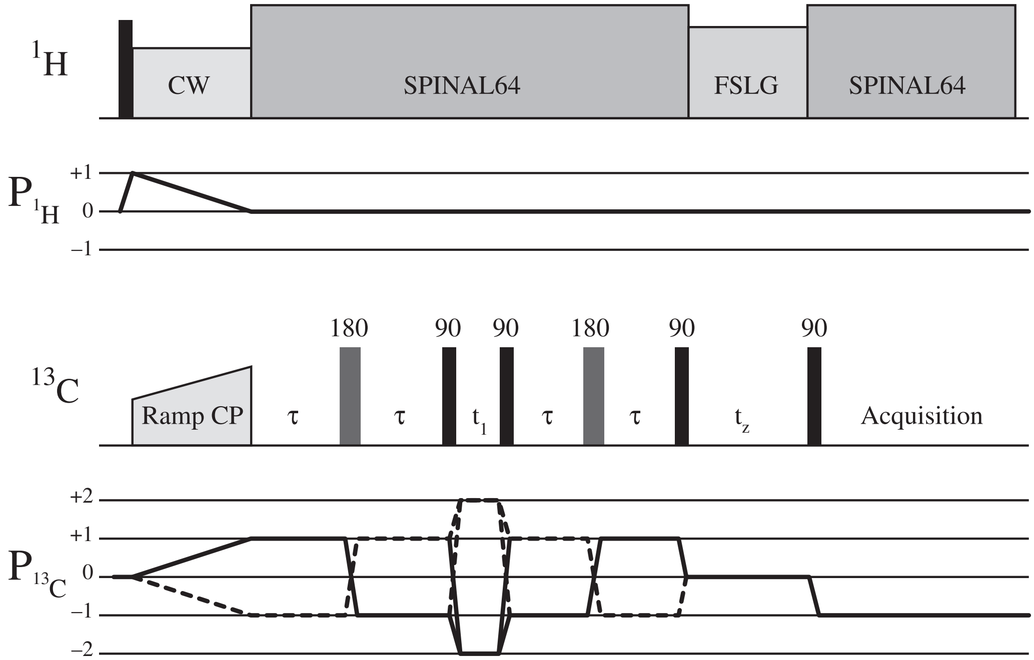

Fig. 1. The pulse sequence used for the FSLG-zfr-INADEQUATE. Notice that the ^{13}C coherence pathway has many allowed paths; however, the two τ–180°–τ periods must have an inversion of the coherence order (−1 to +1 or +1 to −1). Similarly the double quantum coherence may come from either the −1 or +1 coherence. At the end of the sequence both the −1 and +1 coherences may lead to the zero quantum coherence during the z-filter. The FSLG phase was 0°/180° alternating with the frequency shifts every 9.0 μs for our power level.

3. Results and discussion

The results of the variable z-filter experiments (shown in Fig. 2) were as expected, with the longer z-filters producing greater degrees of mixing between adjacent carbon atoms in the molecule at a given double-quantum frequency. When the z-filter was kept short (1 ms), the amount of spin diffusion artifacts were minimized; however, the lineshapes of the peaks still contained residual anti-phase signal resulting from flip-flop terms that can distort the overall phase of the observed peaks.

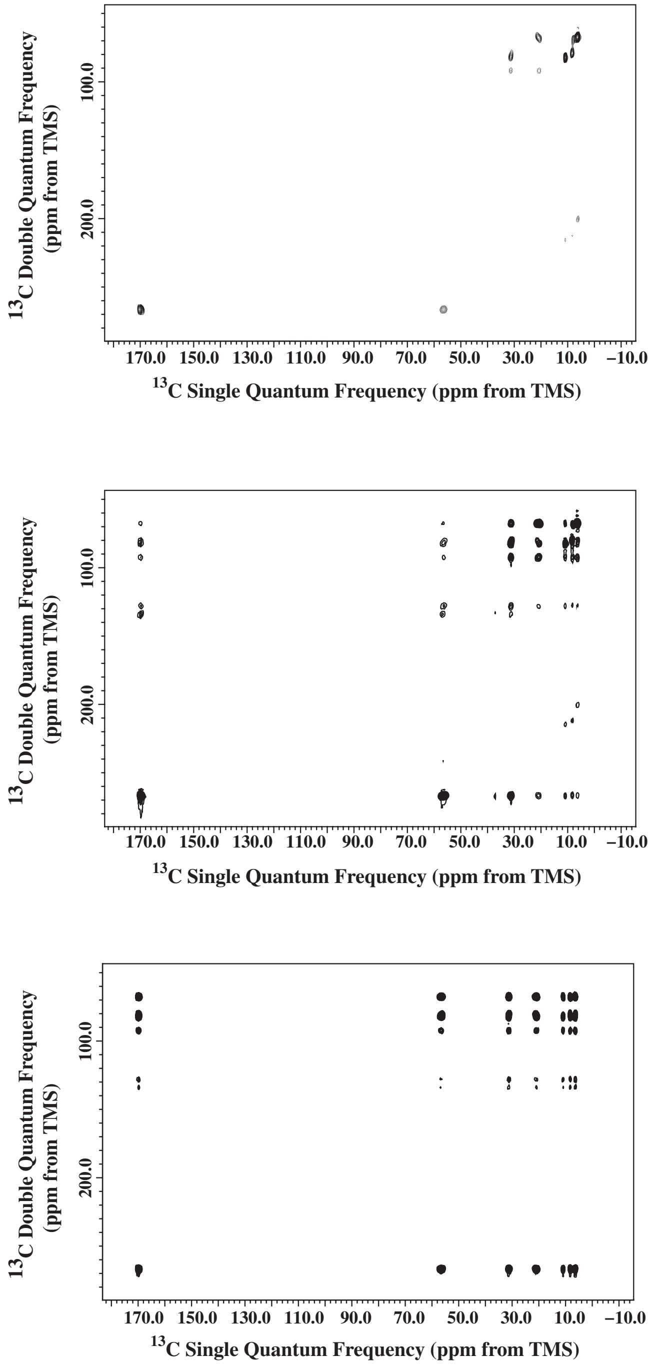

Fig. 2. The three 2D zfr-INADEQUATE spectra were acquired with identical conditions other than the length of the z-filter that was set to 1.5 ms for the top, 6.4 ms for the middle and 25.6 ms for the bottom. It is clear that with both the 6.4 ms and 25.6 ms z-filters significant spin diffusion (SD) is occurring and the number and size of artifact peaks becomes maximal for the long z-filter. A total of 22 contour levels are spaced linearly from 5% to 95% maximum intensity.

As described in previous publications, the spin diffusion occurs when carbon atoms with different frequencies flip simultaneously (converting an $\mathbf{I}_{z,A}$ coherence on spin A into a $\mathbf{I}_{z,B}$ coherence on spin B) [36,37]. This is a nearly zero energy transition that uses the residual heteronuclear dipolar couplings between neighboring hydrogen atoms and the carbon atoms to act as an energy offset to increase the transition probability by making the effective transition frequency closer to zero (so called proton-driven spin diffusion). This does not play a major role in dephasing the homonuclear zero-quantum flip-flop coherences present at the start of the z-filter (specifically the $\mathbf{I}_{+,A}\mathbf{I}_{-,B}$ and $\mathbf{I}_{-,A}\mathbf{I}_{+,B}$ coherences with respect to two adjacent J-coupled carbon atoms A and B). This dephasing is a coherent process that relies on a distribution of energy differences to allow the coherence to effectively evolve into

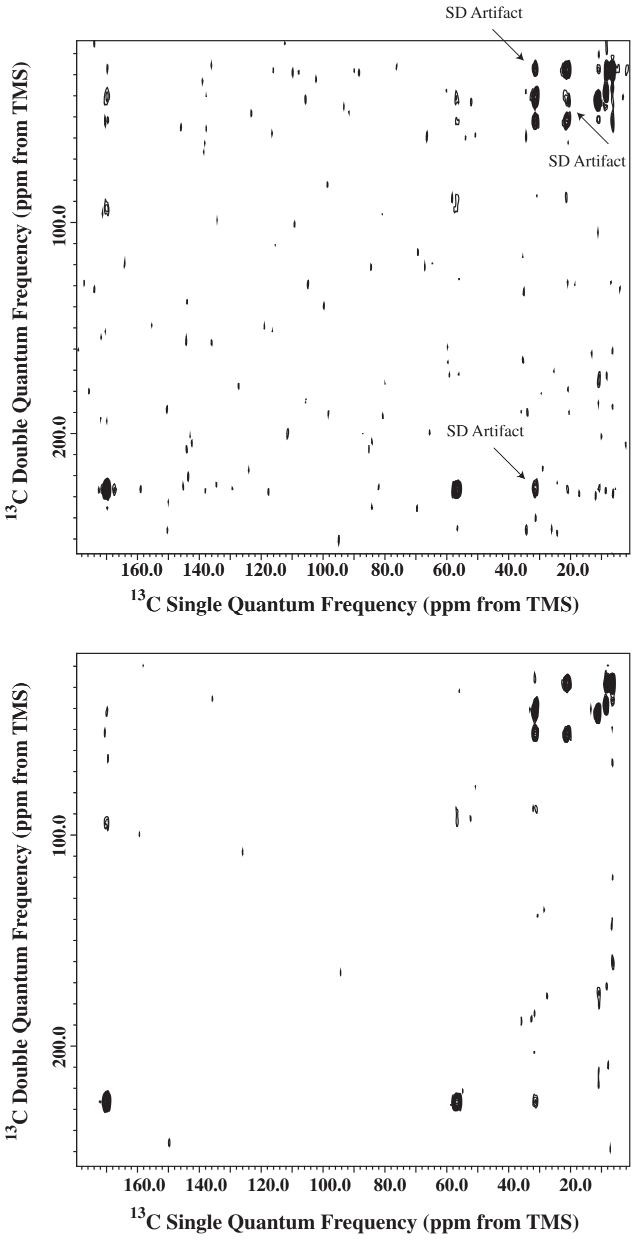

Fig. 3. The 2D FSLG-zfr-INADEQUATE spectrum is shown below the zfr-INADEQUATE spectrum. All other parameters were identical (including the total z-filter time of 4.5 ms) aside from using FSLG during the z-filter in the lower spectrum. The top spectrum shows significantly larger spin diffusion (SD) artifacts than are present in the lower spectrum. A total of 22 contour levels are spaced linearly from 5% to 95% maximum intensity.

the other zero-quantum flip-flop term. Having residual heteronuclear dipolar couplings speeds this process by causing the effective precession frequencies of these coherences to be distributed over a greater range. The longer the z-filter, the greater degree these coherences will essentially be fully dephased; however, the price to be paid is the greater degree of spin diffusion mixing of the desired signals. By applying an FSLG sequence during the z-filter, the homonuclear coupling between ^{1}H atoms will be partially removed. This will help prevent the mixing of these hydrogen spin states by the strong dipolar coupling. This will serve to help reduce one of the mechanisms by which the $\mathbf{I}_{z,A}$ can be transferred coherently to from spin A to spin B as an $\mathbf{I}_{z,B}$ coherence.

At the longest z-filter periods, all of the ^{13}C peaks are fully spin exchanged and no information may be extracted about specific connectivities. As described above, one possible solution to this problem of spin diffusion was to use FSLG homonuclear decoupling during the z-filter to reduce the formation of artifacts. Fig. 3 shows the spectra acquired with and without FSLG decoupling during a 4.5 ms z-filter. The spin diffusion artifact peaks are significantly reduced in the FSLG spectrum as desired. This had the further benefit of maintaining the intensity in the proper peaks in each double quantum slice; thus, increasing the overall signal-to-noise ratio (since signal is not split amongst additional artifact peaks). Fig. 4 shows the projections of three of the double quantum frequencies onto the single-quantum dimension. These spectra give a good indication of the degree to which the FSLG has reduced the artifact signals in each projection. It is possible also that some longer range *J*-coupling is leading to the remaining "artifact" cross-peaks, so it is not clear that these can (or should) ever be completely removed. In all cases the artifacts have been reduced by at least a factor of three and in some cases by a factor of more than ten. The only major drawback of adding FSLG to the z-filter is the increased total

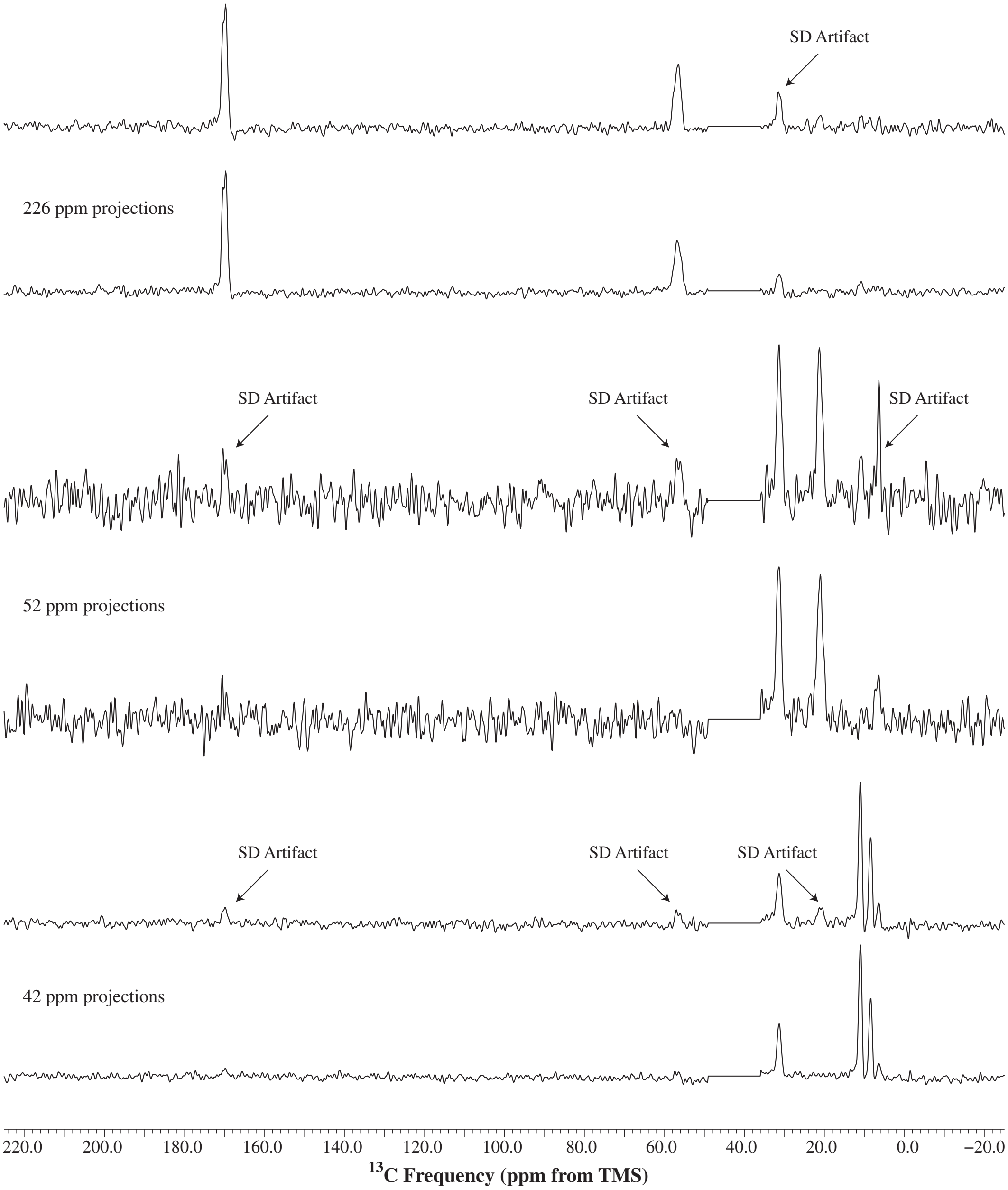

Fig. 4. The six projections represent the sum of slices from ±1 ppm of the listed double-quantum frequency. In each case the lower spectrum is acquired with the FSLG during z-filter and the upper without the FSLG decoupling. The spin diffusion (SD) artifacts are indicated and are generally at least three times larger than in the FSLG version of the experiment and in some cases significantly more.

decoupling (heteronuclear during evolution and detection, and homonuclear during the z-filter) time and potential sample heating that could result. In the original zfr-INADEQUATE, the z-filter served as a period to actually turn off the decoupling field and reduce sample heating. In the FSLG-zfr-INADEQUATE, the decoupling field is on continuously (though set off resonance to fulfill the FSLG conditions); hence, care must be taken to not damage the probe or sample. In most cases the total z-filter time needed to dephase flip-flop terms was rarely more than 10 ms while the acquisition and double-quantum formation/evolution periods was usually much longer (50 ms or longer).

It is possible that other homonuclear decoupling schemes mentioned earlier might work equally well or even better than FSLG. However, given that the FSLG (or equivalent PMLG) are easy to set-up and implement, we chose not to try to examine other decoupling approaches. The conclusion we have reached about using FSLG during the z-filter is that we are not actually trying to get ideal fully resolved ^{1}H spectra or complete homonuclear decoupling, but rather just enough decoupling to reduce the spin diffusion artifacts that occur in the zfr-INADEQUATE. The FSLG approach has proven successful and easy to add to existing pulse sequences when needed. As with the standard zfr-INADEQUATE, choosing the best z-filter time along with adding the FSLG decoupling may be very sample dependant. Some samples might self-decouple the spin diffusion due to internal motions while others might have reduced spin diffusion due to the distribution of protons in the sample itself. The FSLG approach offers a simple way to remediate the artifact problems when the conditions that produce them cannot be eliminated or avoided.

Another alternative that has been explored by Mueller and others [38,39] involves using heteronuclear decoupling to help remove the artifacts that arise from the residual dipolar interactions. We have not compared our experiments to these heteronuclear versions and this may well be worth future study. We believe that leaving only the short range heteronuclear ^{13}C–^{1}H couplings while eliminating the much longer range homonuclear ^{1}H–^{1}H couplings during the z-filter will produce superior performance, since these residual couplings should not lead to artifact cross-peaks but will continue to help dephase the unwanted signals (which is the goal of the z-filter in the first place). However, homonuclear decoupling does require greater care in setup and errors due to various pulse and frequency offset imperfections which may render the homonuclear decoupling less effective overall than the heteronuclear approach. In much the same way there are a range of choices for the type of homonuclear decoupling used, there will be a range of possible heteronuclear decoupling sequences. It is likely that there may be some situations where homonuclear decoupling performs better than heteronuclear decoupling and vice versa. We suggest that in most cases this should be examined on a sample-by-sample basis.

4. Conclusion

It is clear from this work that when spin diffusion is potentially creating artifacts in the 2D zfr-INADEQUATE that the application of some form of homonuclear decoupling may help remove these artifacts. Spin diffusion artifacts are enhanced when the z-filter time period is made long or spinning speeds are slow, but these conditions are not always avoidable. In this work we selected the FSLG, but are confident that other approaches might work if optimized properly. The spin diffusion is of primary importance when the sample spinning is slow enough that the residual ^{1}H–^{1}H dipolar couplings (independent of the size of external magnetic field) are significant. This would be true for MAS probes that spin under 15 kHz, which is inclusive of almost every 5 mm and larger rotor size.

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