Efficient Heteronuclear Dipolar Decoupling in NMR of Aligned Samples at High Fields

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Introduction
Efficient decoupling in solid-state NMR of aligned samples tends to be obscured by strong homonuclear dipole-dipole interactions among abundant protons and by their resonance dispersion over a large chemical shift range. For instance, the anisotropic chemical shift of amide $^1$H resonances spans 14 ppm, with an additional isotropic $^1$H chemical shift dispersion of ~10 ppm. Therefore, the $^1$H resonances could span 24 ppm, corresponding a $^1$H bandwidth of 22 kHz needs to be decoupled on a 21 T magnet (i.e. a 900 MHz spectrometer). A higher static magnetic field means a larger $^1$H chemical shift range that must be covered for decoupling in order to take full advantage of the high fields. So far, the most significant development in heteronuclear dipolar decoupling in NMR of stationary aligned samples was SPINAL (small phase incremental alternation) sequences [1] utilizing two-pulse phase modulation (TPPM) [2] elements in combination with the variation of the phase angles in these TPPM elements is not necessarily zero anymore. This new sequence is called PW-TPPM[3], an acronym for phase-wiggled two-pulse phase modulation, since the TPPM elements become phase-wiggled.

Experimental
The NMR experiments were performed on a Bruker Avance WB600 and the ultra-wide bore 900 MHz NMR spectrometers using low electrical field PISEMA probes with a rectangular coil dimension of 7.6 x 5.6 x 11 mm.

Results and Discussion
Fig. 2 shows the $^{15}$N spectra of the amidated $^{15}$N-$V_{10}G_{13}I_{14}$ p3-NH$_2$ peptide aligned in hydrated lipid bilayers using different decoupling schemes. For these three $^{15}$N resonances at 40.9, 46.8, and 56.4 ppm, their bonded amide proton resonances are 16.0, 9.4, and 11.5 ppm, respectively (spectrum not shown), which corresponded to a decoupling offset of +5.40, -0.54, and +1.35 kHz, respectively. As shown in Fig. 2, with the use of PW-TPPM the proton resonances are 16.0, 9.4, and 11.5 ppm, respectively (spectrum not shown), which corresponded to a decoupling offset of +5.40, -0.54, and +1.35 kHz, respectively. As shown in Fig. 2, with the use of PW-TPPM the signal intensities for the $^{15}$N resonances at 46.8 and 56.4 ppm were improved by about 10%, while the signal intensity at 40.0 ppm was improved by about 35%. Thus, this new sequence proved to have much better decoupling efficiency over a large chemical shift range, allowing us to take more advantage of high fields for biological solid-state NMR studies of membrane bound proteins and peptides aligned in hydrated lipid bilayers. Theoretical analyses [3] indicate that such phase wiggling introduces a time-dependence that causes a resonance for additional averaging of the residual heteronuclear dipolar interactions in stationary solids leading to the significant improvement on decoupling efficiency over a large bandwidth.

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References