Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information for *A common theory of phase-modulated homonuclear decoupling in solid-state NMR*

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A. Calculating the quality factor

The quality factor, q, used to quantify the apparent decoupling efficiency in ^{1}H 1D solid-state NMR spectra of powdered β-AspAla, acquired with windowed decoupling, was the sum of peak intensities multiplied by the chemical shift scaling factor.

$$q = \lambda_{CS}\left(I_{CH_3} + I_{NH_3} + \sum_{n=1}^{N} I_n \right) \tag{1}$$

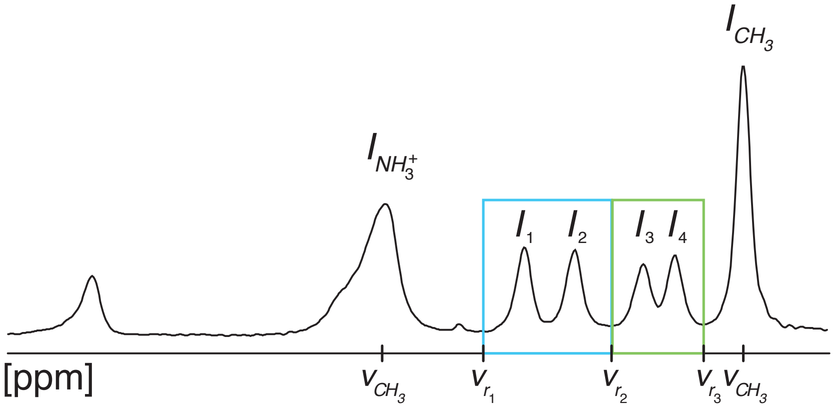

Figure 1 An example ^{1}H spectrum of β-AspAla. The two most intense peaks are assigned to the CH_3 and NH_3 resonances. The CH and CH_2 resonances are located in the regions highlighted in blue and green, respectively.

An effort was made to prevent the misidentification of artefacts as peaks by using the following procedure.

1. Run a peak picking routine to obtain a peak list.
2. From the peak list, identify the two largest peaks in the spectrum and assign their intensities to: I_{CH_3} and $I_{NH_3^+}$, and their frequencies to: ν_{CH_3} and $\nu_{NH_3^+}$.
3. Calculate the scaling factor, λ_{CS}, using eqn (2).

$$\lambda_{CS} = \frac{\Delta\nu_{uncorr}}{\Delta\nu} = \frac{\nu_{CH_3} - \nu_{NH_3^+}}{6.6\,\text{ppm}} \tag{2}$$

4. Determine the regions of the spectrum (uncorrected by the scaling factor) where the CH ($\nu_{CH} \in \left[\nu_{r_1}, \nu_{r_2}\right]$) and CH_2 ($\nu_{CH_2} \in \left[\nu_{r_2}, \nu_{r_3}\right]$) resonances should be found by using eqn (3) and the reference values: $\nu_1 = 4.5$ ppm, $\nu_2 = 2.5$ ppm, and $\nu_3 = 0.8$ ppm.

$$\nu_{r_n} = \nu_{CH_3} + \nu_n \lambda_{CS} \tag{3}$$

5. From the peak list, assign a maximum of two peaks in each of the CH and CH_2 regions of the spectrum to the variables: I_n.
6. Calculate the quality factor using eqn (1).

B. Legendre coefficients

	PMLG	eDUMBO-1_{22}	ePMLG	ePMLG^D
c_0	variable	+0.1356	-0.0570	-0.1413
c_1	±0.2887	-0.3037	+0.2732	+0.3362
c_2	-	-0.1196	-0.0223	+0.0105
c_3	-	+0.1366	-0.0133	+0.0523
c_4	-	-0.0492	+0.0606	+0.0067
c_5	-	+0.2373	-0.0910	-0.0290
c_6	-	+0.0561	+0.1039	+0.0147
c_7	-	-0.0483	+0.0459	-0.0410
c_8	-	-0.0235	+0.0225	-0.1068
c_9	-	-0.0323	+0.0877	-0.1003
c_{10}	-	+0.0081	-0.0360	+0.0351
c_{11}	-	+0.0185	-0.0050	+0.0120
r_0	-	-	+0.6073	+0.3005
r_1	-	-	+0.0263	+0.0047

C. T_2' fitting parameters

				PMLG			
	CH_3	CH_2^a	CH_2^b	CH^{asp}	CH^{ala}	NH_3^+	OH
T_2' (ms)	5.2	3.6	3.3	5.3	6.9	3.6	7.5
G (%)	6	0	0	19	31	2	31
				eDUMBO-1_{22}			
	CH_3	CH_2^a	CH_2^b	CH^{asp}	CH^{ala}	NH_3^+	OH
T_2' (ms)	8.4	6.5	6.0	7.5	11.1	4.5	9.3
G (%)	21	15	10	46	37	0	43
				ePMLG			
	CH_3	CH_2^a	CH_2^b	CH^{asp}	CH^{ala}	NH_3^+	OH
T_2' (ms)	5.7	3.7	3.4	6.1	7.7	3.2	8.1
G (%)	15	0	1	46	51	0	57
				ePMLG^D			
	CH_3	CH_2^a	CH_2^b	CH^{asp}	CH^{ala}	NH_3^+	OH
T_2' (ms)	10.2	8.1	8.2	9.6	13.2	5.3	11.8
G (%)	18	14	27	58	63	2	50

D. RF offset compensation with extra phase modulation

As discussed in section 5 of the text, an extra phase modulation was used during the experimental optimizations to render the optimization process less sensitive to non-ideal RF offset values. This effect can be explained by considering the effect of phase transients on homonuclear decoupling.

It is well established[1, 2] that RF inhomogeneity in combination with asymmetric phase transients give rise, in practice, to a dependence of decoupling performance on the RF offset. As shown by Vega,[2] this is due to spectral broadening that results from a range of chemical shift scaling factors across the sample. This range of scaling factors is due to RF inhomogeneity. In the absence of phase transients, this broadening is minimized for on-resonance RF irradiation. However, phase transients shift the frequency at which minimum broadening is achieved.

The extra modulation used in our experimental optimizations is a rapid phase ramp, which will give rise to a large asymmetric phase transient.[2] We hypothesize that this phase transient acts to shift the RF offset at which minimum broadening is achieved. To support this proposition we present a series of spectra acquired with the ePMLG sequence with the extra modulation (Figure 2a) and without the extra modulation (Figure 2b). If we compare the spectra in Figure 3a and Figure 3b, we find that by removing the extra modulation from the ePMLG waveform the quality of the spectrum is significantly reduced. However, as shown in Figure 3c, a spectrum of the same quality can be recovered by changing the RF offset frequency.

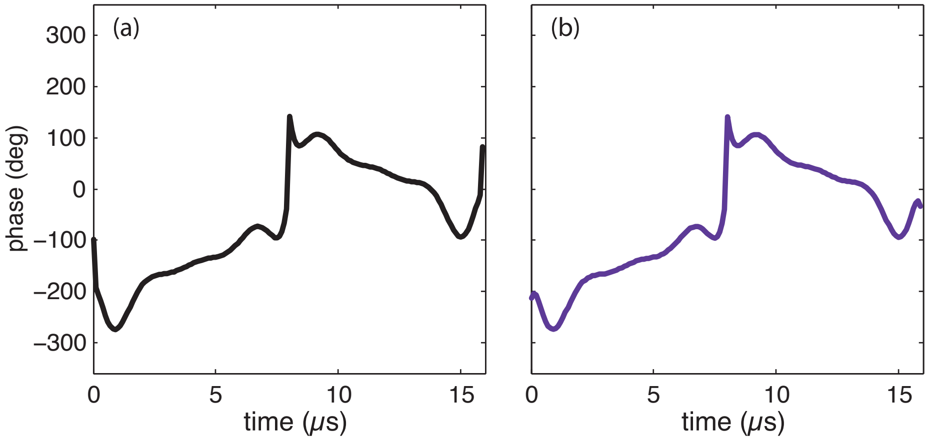

Figure 2 Phase modulation waveforms for the ePMLG sequence (a) with the extra initial ramp modulation and (b) without the extra initial ramp modulation.

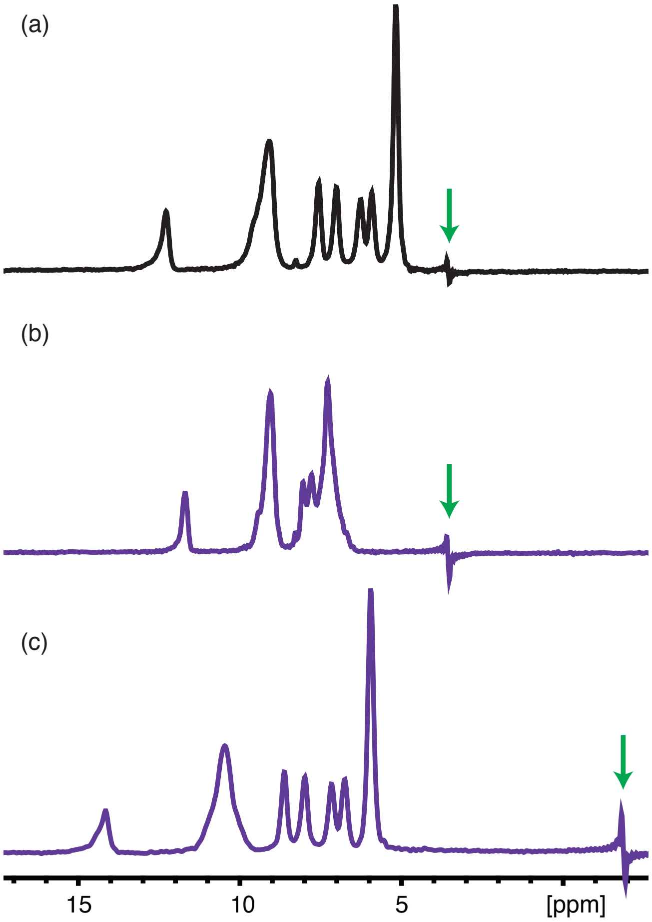

Figure 2 1D ^{1}H NMR spectra of β-AspAla acquired in a windowed fashion using (a) the ePMLG phase waveform with the extra phase modulation (Figure 3a) and an RF offset of -3.3 kHz, (b) the ePMLG phase waveform without the extra phase modulation (Figure 3b) and an RF offset of -3.3 kHz, (c) the ePMLG phase waveform without the extra phase modulation (Figure 3b) and an RF offset of -7.4 kHz. The green arrows highlight the artefact at the RF offset frequency in each spectrum. These spectra have not been corrected by the chemical shift scaling factor.

References

1. L. Bosman, P. K. Madhu, S. Vega and E. Vinogradov, *J. Magn. Reson.*, 2004, **169**, 39-48.
2. A. Vega, *J. Magn. Reson.*, 2004, **170**, 22-41.