Fast REDOR with CPMG Multiple-Echo Acquisition

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Introduction

Rotational Echo Double Resonance (REDOR)[1] is a powerful and widely used experiment for measuring distances of hetero-nuclear spin pairs. REDOR measurement is usually carried out in a point-by-point manner by varying the dipolar dephasing time. In this report, we present a scheme for speeding up the REDOR experiment based on Carr-Purcell Meiboom-Gill (CPMG) sequence.[2,3] The multiple-echo acquisition allows for a complete REDOR curve measured in real-time fashion. This ultrafast method[4] is applicable mostly for measuring mid- to long-range distances since the long dipolar evolution times required for measuring weak couplings allow echo windows that are sufficiently large for chemical shift resolution.

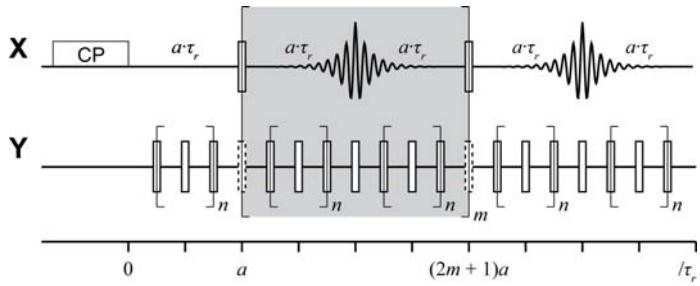

Fig. 1 Schematics of the CPMG/REDOR pulse sequence, where τ_r denotes the rotor period. The integers *a*, *n* and *m* determine the total dipolar evolution/dephasing time; $n = a - 1$ and $2a\cdot\tau_r$ is the duration of the CPMG echo acquisition windows. The S_r and S_0 experiments are acquired with and without pulses on the Y channel, respectively.

Experimental

Experiments were performed on the NHMFL ultra-wide bore 21.1 T superconducting magnet with a Bruker Avance III 900 spectrometer and a 3.2 mm low-E MAS probe designed and built at the NHMFL. ^{13}C-observed spectra were acquired at 10 kHz MAS with ^{13}C and ^{15}N *rf* fields of 83 and 50 kHz, respectively, and 100 kHz SPINAL-64 ^{1}H decoupling.

Results and Discussion

The pulse sequence in Fig. 1 shows CPMG multiple echo acquisition (X-channel) under dipolar recoupling (Y-channel). The continuous recoupling allows for real-time measurements of the REDOR curve via data acquisition between the refocusing pulses as indicated by the echoes. Fig. 2 shows the result of a complete ^{13}C{^{15}N} REDOR curve for the CH_3 site of [^{15}N]alanine acquired in the ultrafast fashion with a total of 4 scans. It should be mentioned that the conventional REDOR experiment acquires only one point on the curve at a time. Fig. 2 also shows that it is necessary to use XY-8 phase cycling[5] of the CPMG pulse to compensate the effects of imperfect π-pulses. Without the compensation, the REDOR curves tapers off at a lower plateau (red open circles) as compared to the compensated data (black dots) and universal REDOR curve (solid line).

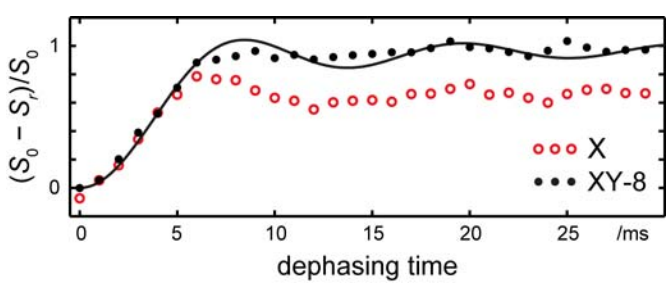

Fig. 2 ^{13}C{^{15}N} REDOR curves for the CH_3 site of [^{15}N]alanine collected with constant (red open circles) and XY-8[5] (black filled circles) phase cycling of the CPMG refocusing pulse. The REDOR curves were each acquired with only a total of four transients (two for S_0 and two for S_r). A universal REDOR curve corresponding to a ^{13}C-^{15}N distance of 2.5 Å is shown as a black line.

Conclusions

Incorporating CPMG multiple-echo acquisition can speed up REDOR experiments. The gain in time-efficiency from using CPMG/REDOR is most dramatic when measuring mid- to long-range distances, and in the presence of large inhomogeneous line-broadening.

Acknowledgements

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References

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