Development of State-of-the-Art Solid-State NMR Methods Suitable at Ultrahigh Magnetic Fields and Ultrafast MAS Spinning Rates

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Introduction

A novel method for achieving two-dimensional (2D) ^{13}C-^{13}C exchange spectroscopy under fast magic-angle spinning (MAS) rates ($\nu_r \gtrsim 40$ kHz) relying on a low power adiabatic chirp pulse mixing scheme, has been developed and demonstrated. The reason for developing such broadband ^{13}C-^{13}C homonuclear dipolar recoupling methods under fast MAS spinning rates while employing low rf pulses, is that conventional methods such as PDSD[1] or DARR,[2] popular under low MAS spinning rates, do not work well at fast spinning rates and in the presence of wide offset distributions. Moreover, other rf-pulse driven recoupling methods that are operational under an ultrahigh MAS spinning rate often possess the drawbacks of requiring strong rf pulses, which is both a burden on the probe and a major cause of heat generation in the sample that is particularly disadvantageous for studying biological samples at high fields.

Experimental

A pulse scheme of the standard ^{13}C-^{13}C exchange spectroscopy was adopted and endowed with an adiabatic chirp pulse mixing with a low rf pulse power along the ^{13}C channel and simultaneously a low power pulse along ^1H channel satisfying $\nu_1(^1H) + \nu_1(^{13}C) = \nu_r$, a double-quantum (DQ) Hartman-Hahn matching condition.[3] Under fast MAS spinning rates this corresponds to a proton-assisted ^{13}C-^{13}C recoupling method that greatly alleviates the dipolar truncation effect,[4] allowing to detect effectively long distances among (> 5 Å) ^{13}C-^{13}C pairs, even in the presence of the strong directly bonded ^{13}C-^{13}C dipolar pairs in uniformly ^{13}C-labeled biological samples.

Results and Discussion

Shown in Figure 1 is a demonstration of the method's efficiency using a 2D ^{13}C-^{13}C exchange NMR experiment at a MAS

Fig.1 Pulse sequence (top), 2D rf pulse simulation map (A), and 2D ^{13}C-^{13}C NMR spectrum measured on [U-^{13}C]Tyrosine (B) of the new method.

rate ν_r = 60 kHz. It shows the pulse scheme, a simulation map for finding the optimal rf pulse strengths, and an experimental result measured on [U-^{13}C]Tyrosine. Panel (A) shows a well-defined DQ mixing mode arising along the dashed diagonal line (from the upper left-hand to the bottom right-hand corner), satisfying the $\nu_1(^1H) + \nu_1(^{13}C) = \nu_r$ condition.[5] Panel (B) shows how all the carbon sites that are present in [U-^{13}C]Tyrosine exhibit a total correlation (mixing time τ = 7 ms). We are currently extending its application to uniformly or selectively ^{13}C-labeled proteins for assessing its competitiveness in real bioloical applications.

Conclusions

A novel method was successfully implemented for acquiring solid-state ^{13}C-^{13}C exchange NMR spectrum of a uniformly labeled sample with a suppressed dipolar truncation effect under an ultrahigh MAS spinning rate while employing low rf pulse powers.

Acknowledgements

References

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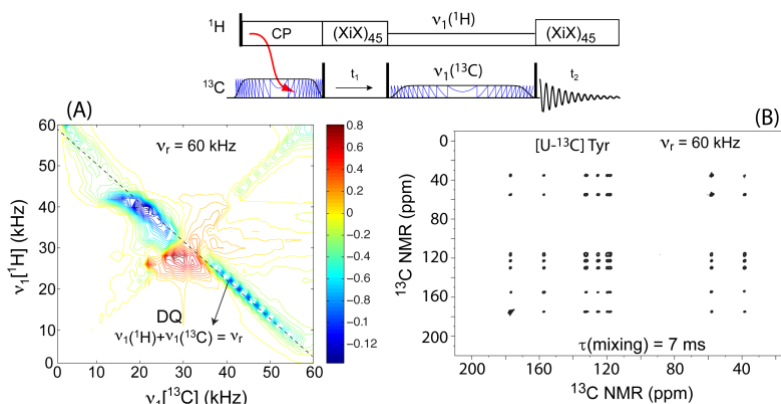[5] Wi, S., *et al.*, J. Chem. Phys., **142**, 064201 (2015).