PROTON-DETECTED $^{14}$N MAS NMR USING HOMONUCLEAR DECOUPLED ROTARY RESONANCE

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Introduction

Indirect detection through proton can in principle enhances the sensitivity dramatically especially for low-$\gamma$ nuclei like $^{14}$N. However, proton $T_2$ is usually short in rigid solids and can offset the sensitivity gain. There are two ways to reduce this $T_2$ loss: either making the $T_2$ longer or using the largest coupling possible for the coherence transfer. We report here homonuclear decoupled rotary resonance for $^1$H/$^{14}$N HMQC in solids. By using the so-called $n=2$ rotary resonance, the $^1$H/$^{14}$N heteronuclear dipolar interaction is efficiently recoupled under MAS while the proton homonuclear dipolar interactions remains decoupled maintaining long $T_2$.

Experimental

The $^1$H/$^{14}$N double-resonance experiment was performed on a Bruker Avance-800 spectrometer at the University of Lille, France with a 3.2 mm magic-angle spinning probe.

Results and Discussion

Figure 1 shows the $^1$H/$^{14}$N HMQC pulse sequences. The $^1$H/$^{14}$N dipolar recoupling is achieved with a simple rotary resonance scheme with rf field matching twice of the spinning frequency. The $n=2$ rotary resonance recouples only the heteronuclear dipolar and CSA interactions but not the homonuclear dipolar coupling due to its bilinear nature of spin operators. The CSA is refocused with the $\pi$-pulse in the middle leaving only the heteronuclear dipolar coupling for $^1$H/$^{14}$N HMQC. There are a couple of advantages of using rotary resonance. First, the cw recoupling is simple and susceptible to spinning frequency fluctuation. Second, the proton $T_2$ is not shorten by the rf. In fact, we have found that proton $T_2$ under rotary resonance is even longer than that under plain MAS. The 2D spectrum of glycine shows $^1$H/$^{14}$N correlations with 400μs coherence transfer. The proton $T_2$ loss is less than 50% for this mixing time which already reaches the steady state for NH$_3$. For the long range correlation from the CH$_2$ proton, the coherence transfer is still in the initial build-up. Nevertheless, the signal intensity is still evident from the shoulder on the right.

Conclusions

$^1$H/$^{14}$N HMQC spectra can be obtained efficiently with the $n=2$ rotary resonance dipolar recoupling. Such an experiment gains sensitivity from the more sensitivity proton detection and near 100% proton natural abundance at the cost of some resolution as compared to $^{13}$C detected HMQC method.

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References