Indirect Detected ^{14}N Wide Line NMR under MAS

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Introduction

It has been shown recently that indirect detection through ^{13}C or ^{1}H under magic-angle spinning can overcome the resolution and sensitivity difficulties of observing ^{14}N in solid state [1,2]. The enhanced spectral resolution and sensitivity open up new opportunities for ^{14}N NMR with its ~100% natural abundance and quadrupolar coupling parameters inaccessible through ^{15}N. The HMQC-type 2D experiment [1,2] averages the large first-order ^{14}N quadrupolar interaction with rotor-synchronized t_1 and accurate magic-angle setting. The quadrupolar coupling parameters are obtained by fitting the remaining second-order quadrupolar shift along the indirect dimension. We present here a wide line approach for measuring ^{14}N quadrupolar coupling by replacing the ^{14}N frequency-encoding with a long pulse [3].

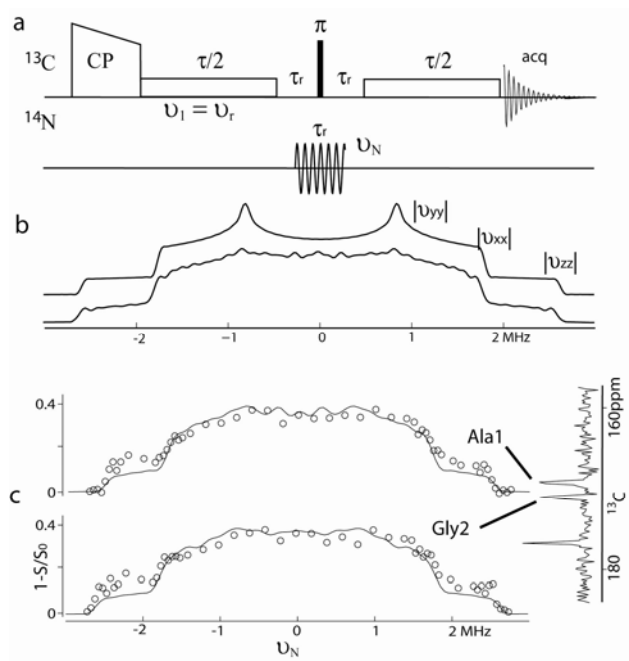
Experimental

All measurements were performed using a Bruker 600MHz wide bore instrument at the NHMFL with a 4mm triple resonance magic-angle spinning probe.

Results and Discussion

Figure 1a shows the pulse sequence using rotary resonance recoupling for indirect detection. The simulations in Figure 1b shows that the three principal components υ_x, υ_y and υ_z of the quadrupolar coupling tensor can be picked out easily from the wide line spectra. Figure 1c demonstrates this experiment using a natural abundant tri-peptide Ala.Gly.Gly. The results and simulations show that the scanning ^{14}N frequency is very similar to the static first-order quadrupolar lineshape allowing accurate measurement of the quadrupolar coupling parameters. The ^{14}N quadrupolar spectra are resolved by ^{13}C chemical shift and their fitting yields quadrupolar coupling parameters C_q=3.48MHz, η=0.368 for Ala1 and C_q=3.35MHz, η=0.373 for Gly2. The efficiency of the experiment is improved over the HMQC-type experiment by a level-crossing mechanism. The modulation of quadrupolar coupling during the rotor-period long pulse brings the r.f. irradiation on-resonance such that r.f. action covers all spins despite that the quadrupolar coupling is two orders of magnitude over larger than the r.f. field stength. The optimal r.f. field has been found with the adiabaticity parameter

$$\alpha = \upsilon_1 / (\upsilon_q \upsilon_r)^{1/2} \approx 0.25 \qquad [1]$$



Conclusions

The wide line approach has the advantage of better accuracies and higher efficiencies over the HMQC-type experiment for measuring ^{14}N quadrupolar coupling especially with large coupling constants.

Acknowledgements

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References

[1] Gan Z., *J Am Chem Soc*, 128 6040-6041 (2006).
[2] Cavadini, et al, *J Am Chem Soc* 128 7706-7707 (2006).
[3] Gan Z., *Chem. Comm.* In press.