HIGH-RESOLUTION $^{14}$N/$^{13}$C CORRELATION FOR MEASURING $^{14}$N QUADRUPOolar COUPLING

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Introduction

Nitrogen atoms constitute one of the most important elements in organic, inorganic and biological molecules. In the past, most nitrogen NMR spectroscopy has been carried out with the low abundant isotope $^{15}$N (0.37%) for its favorable NMR properties of a spin-1/2 while the more abundant $^{14}$N isotope (99.6%) has been rarely studied. $^{14}$N NMR spectroscopy suffers from poor sensitivity and broad lines due to the low-$\gamma$ properties and large quadrupolar interaction, nevertheless the $^{14}$N quadrupolar coupling has great potential. This report presents a two-dimensional $^{14}$N/$^{13}$C correlation NMR experiment using the $J$ and residual dipolar couplings under magic-angle spinning for the indirect detection of $^{14}$N NMR spectra. The experiment and the measurement of amide nitrogen quadrupolar couplings are demonstrated with a natural abundant polypeptide.

Experimental

The experiment was performed on a 600MHz wide bore magnet at the NHMFL equipped with a Bruker DRX console. A 2.5mm triple-resonance magic-angle spinning probe was used for the measurement. Other experiment details were: 15ms $\tau$, 25kHz MAS, 16 $t_1$ increments, 8K scans, 2$\mu$s $^{14}$N pulse with a 50kHz RF field, SPINAL64 $^1$H decoupling with 125kHz RF field.

Results and Discussion

Figure 1a shows the HMQC-type pulse sequence for the $^{14}$N/$^{13}$C correlation by scalar $J$ and residual dipolar coupling under magic-angle spinning. The scalar coupling is ~5-11Hz and the second-order quadrupolar-dipolar coupling is about 30Hz at 14.1T. For a complete average of the large first-order quadrupolar coupling, the $^{14}$N evolution time $t_1$ must be rotor-synchronized with the spinning axis precisely at the magic-angle. Figure 2 shows the 2D $^{14}$N/$^{13}$C spectrum of natural abundant tri-peptide Ala-Gly-Gly. The $^{14}$N peaks show a large shift (up to 500ppm) from their chemical shifts measured by a $^{15}$N CPMAS experiment. The differences between $^{14}$N and $^{15}$N peaks come from the isotropic second-order quadrupolar shift, $\delta_{\nu}^{Qiso} = (3 / 40)\left(C_{g} / \nu_{N}^{3}ight) \left(1 + \eta^{2} / 3\right)$.

A precise measurement of this second-order shift leads to the determination of quadrupolar coupling constants, 3.45, 3.32, 1.31MHz, respectively for the three nitrogens in the tri-peptide.

Conclusions

The high spectral resolution and sensitivity of indirect $^{14}$N detection through $^{13}$C enable us for the first time to measure and to use the nitrogen quadrupolar coupling in complex molecules to probe local structure and dynamics.