Accurate determination of C-H and N-H distances for unlabeled molecules by ultrafast solid-state NMR spectroscopy

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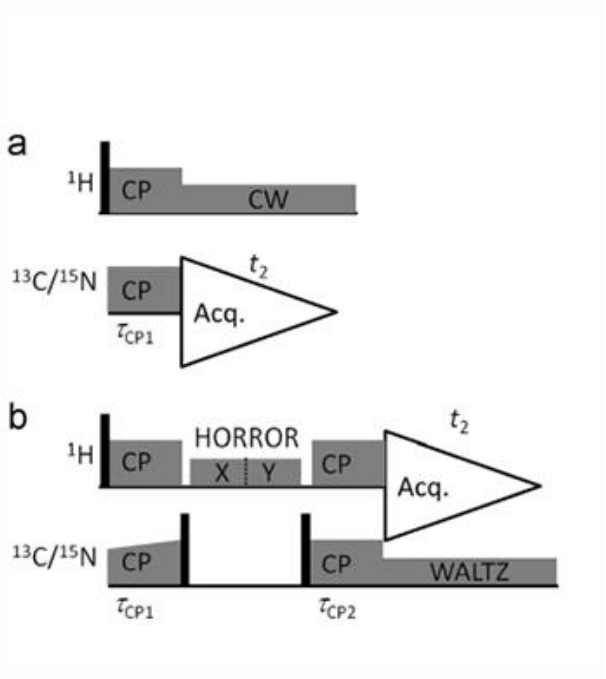
Cross-Polarization with Variable Contact-time (VC-CP) experiment has been used to measure dipolar interactions corresponding to C-H and N-H distances in solid samples [1]. If the VC-CP experiment using direct ^{13}C or ^{15}N detection (Fig. 1a) is performed at Magic Angle Spinning (MAS) at spin rates exceeding 60 kHz, it allows accurate measurement of dipolar distances [2,3]. However, if the pulse sequence is extended in such a way that ^{1}H signal is detected (Fig. 1b), a S/N gain of approx. 2.5 or a time gain of approx. 6 can be obtained [4]. This is demonstrated on U-[^{13}C, ^{15}N] L-alanine in Fig. 2. Spectra shown in Fig. 2a and Fig. 2b were recorded with ^{13}C detection, while spectra in Fig. 2c and Fig. 2d were recorded with ^{1}H detection [4].



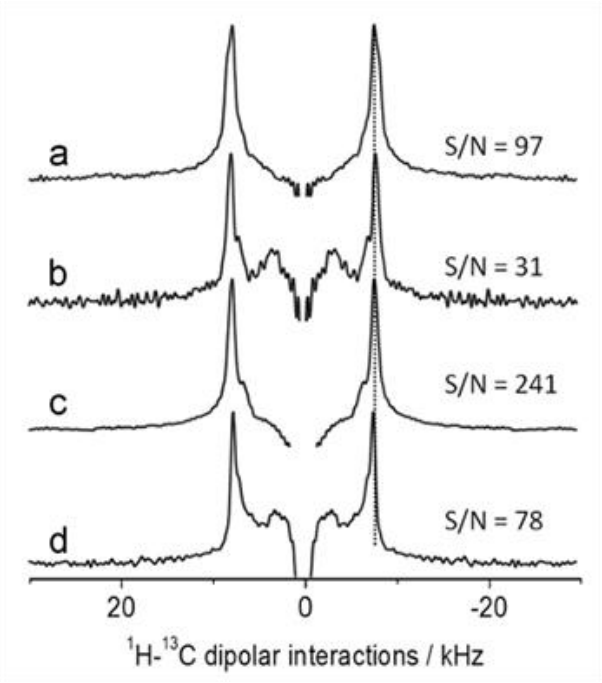


Fig.1 CP-VC pulse sequences with (a) $^{13}C/^{15}N$ detection, or (b) ^{1}H detection.

Fig.2 Slices taken in 2D CP-VC spectra of U-[^{13}C, ^{15}N] L-alanine recorded with ^{13}C (a, b) or ^{1}H (c, d) detection, and (a, c) 70 kHz or (b, d) 100 kHz MAS. Only the peak at 3.6 ppm (^{1}H) is shown.

The sensitivity of ^{1}H detected VC-CP experiment at ultrafast MAS is high enough so that samples at natural ^{13}C and ^{15}N could be measured. This is clearly evidenced on ^{13}C, ^{15}N-natural abundance L-histidine·HCl·H2O in Fig. 3 (^{1}H-^{13}C) and Fig. 4 (^{1}H-^{15}N). The spectra also demonstrate another advantage of ultrafast MAS which is resolved ^{1}H resonances of small organic molecules [4].

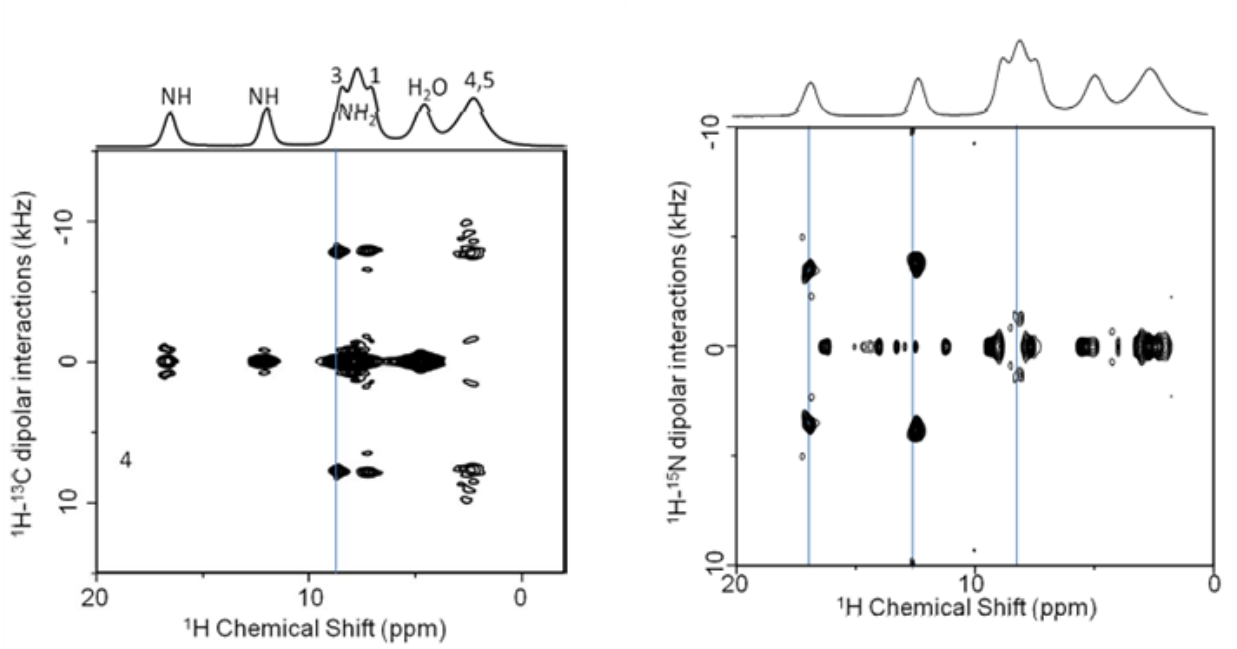


Fig.3 2D CP-VC H-C-H spectrum of ^{13}C-natural abundance L-histidine·HCl·H_2O recorded at 70 kHz MAS. The ^{1}H MAS spectrum is shown on top.

Fig.4 2D CP-VC H-N-H spectrum of ^{15}N-natural abundance L-histidine·HCl·H_2O recorded at 70 kHz MAS. The ^{1}H MAS spectrum is shown on top.

References

[1] P. Paluch, T. Pawlak, J.P. Amoureux, M.J. Potrzebowski, *J. Magn. Reson*. **233** (2013) 56–63.

[2] P. Paluch, J. Trébosc, Y. Nishiyama, M.J. Potrzebowski, M. Malon, J.P. Amoureux, *J. Magn. Reson*. **252** (2015) 67-77.

[3] Application Note NM140017 (http://www.j-resonance.com/en/application/?appid=NM-140017) .

[4] Y. Nishiyama, M. Malon, M.J. Potrzebowski, P. Paluch, J.P. Amoureux, *Solid State Nucl. Magn. Reson*. **73** (2016) 15-21.