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

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$_2$O 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$_2$O recorded at 70 kHz MAS. The $^1$H MAS spectrum is shown on top.

References


