High-resolution solid-state $^1$H MAS NMR of supramolecular materials

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Solid-state NMR of protons has been a long-standing challenge to NMR spectroscopists due to the relatively poor spectral resolution arising from the narrow $^1$H chemical shift range and the strong $^1$H–$^1$H homonuclear dipolar interactions present in most materials. However, these challenges are being met by advances in magic-angle spinning (MAS) technology, the development of advanced pulse sequences, and the availability of high magnetic fields (see Figure 1). Since the linewidths in $^1$H MAS spectra are approximately inversely proportional with MAS frequency, the availability of probes capable of achieving fast MAS conditions (~35 kHz), and now even ultrafast MAS conditions (~70 kHz), offers increased resolution in $^1$H MAS NMR spectra. Furthermore, the ability to perform solid-state $^1$H NMR experiments at ultrahigh-fields offers a further gain in spectral resolution since the chemical shift interaction scales linearly with magnetic field strength, while the $^1$H–$^1$H dipolar interaction remains constant.

Figure 1: Improving in the resolution of $^1$H MAS NMR spectra by increasing the magnetic field strength [1] (left), increasing the magic-angle spinning frequency (middle), or by employing a multiple pulse decoupling sequence (right).

We have been implementing and developing advanced NMR multiple pulse sequences that decouple the $^1$H–$^1$H homonuclear dipolar interactions in order to obtain high resolution $^1$H solid-state NMR spectra [2], with a view towards applications involving structural studies of supramolecular materials. One area of interest is the hydrogen bonding interactions that hold supramolecular materials together. We have developed a new pulse sequence that provides detailed information about hydrogen bonding by measuring the $^1$H chemical shift anisotropy (CSA) while still retaining the high resolution necessary to resolve multiple proton sites [3] (Figure 2). We have also implemented multi-
dimensional NMR experiments [4] that probe the spatial proximities between protons in supramolecular host-guest materials, providing important information about these structures (Figure 3). Finally, we have been performing ab initio calculations of $^1$H chemical shifts in order to complement experimental NMR data. A particularly interesting system has been the complexation-induced $^1$H chemical shifts in calixarene host-guest complexes.

References