

## V-T Development of Shaped Pulse Solid-State NMR Spectroscopy

Shaped radio frequency (rf) pulses are commonly employed in a solution high-resolution nuclear magnetic resonance (NMR) spectroscopy. They are used for selective excitation in multidimensional NMR experiments and broadband spin decoupling for resolution enhancements. However, they are less applied to solid state NMR experiments where the samples usually have much larger spectral widths than those of solution-state samples. In metallic or magnetic materials, the spin-echo method is still employed and only shifts and relaxation data are analyzed. Modern NMR techniques as a multiple quantum NMR provides a correlation of spin interactions between two nuclei, which seems to be very important even in these solid materials. We are currently developing a waveform generator and a transmission line probe, which enable excitations and detections of nuclear spins over a large spectral range.

### V-T-1 Shaped Pulse Solid-State NMR Experiment

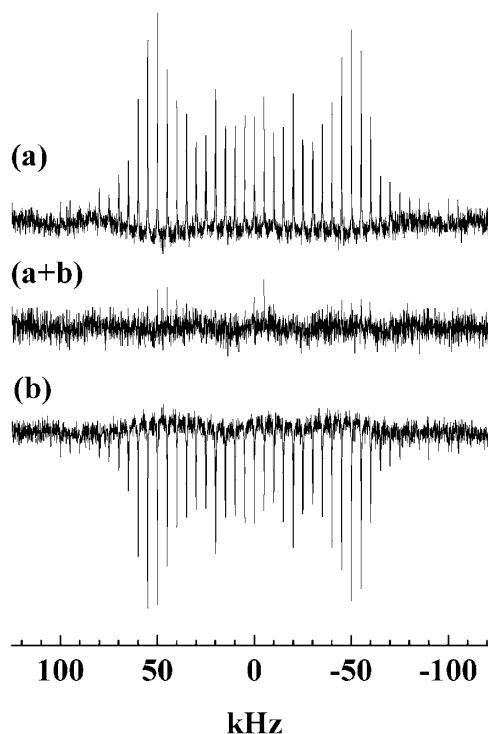
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Shaped radio frequency (rf) pulses are commonly employed in a solution high-resolution nuclear magnetic resonance (NMR) spectroscopy. However, they are less applied to solid state NMR experiments where the samples usually show much larger spectral widths than those of solution-state samples. We have developed a fast wave form generator which could be employed for solid state shaped pulse experiments. Although the circuit was wired by cables on universal printed circuit boards, it worked stable to a clock frequency of 30 MHz. The waveform generator can be controlled by TTL signals from a spectrometer, and it can generate four different shaped pulses. We would like to publish our design elsewhere. We are also currently developing a transmission line probe,<sup>1)</sup> which may enables the broadband excitation of heavily broadened solid-state NMR spectra such as <sup>195</sup>Pt NMR of Pt nanoparticles. However, here we will demonstrate that the waveform generator is also useful in the experiments with an ordinary commercial NMR probe. Figure 1 (a) shows a <sup>2</sup>H solid-state magic-angle spinning NMR spectrum of a rigid deuterium sample with a quadrupole coupling of 160 kHz. An adiabatic inversion pulse WURST20<sup>2)</sup> was applied before the conventional observation pulse sequence and the result is shown in (b). The magnetization was inverted almost completely compared with (a), although the rf pulse amplitude was only 56 kHz. When a rectangular pulse with the same rf strength was used, only 40% of the magnetization were inverted. We conclude that adiabatic pulses may be promising, if it is difficult to obtain enough rf field

strength, especially in triple-resonance experiments.

### References

- 1) Conradi, M. S., *Concepts Magn. Reson.* **5**, 243 (1993).
- 2) Kupce, E.; Freeman, R., *J. Magn. Reson. A* **118**, 299 (1996).



**Figure 1.** The inversion efficiencies of a <sup>2</sup>H magnetization by an adiabatic pulse, WURST20. (a) <sup>2</sup>H MAS NMR spectra of 2,2'-thiobis[5,5'-dimethyl-3-hydroxy-2-cyclohexen-1-one]-d<sub>2</sub>. In (b), the magnetization was inverted by a WURST20 with length of 64 μs and a rf amplitude of 56 kHz. The rf frequency was swept during the pulse from -200 kHz to +200 kHz.

## V-U Development of <sup>13</sup>C High-Resolution NMR Spectroscopy for Nematic and Cholesteric Liquid Crystals

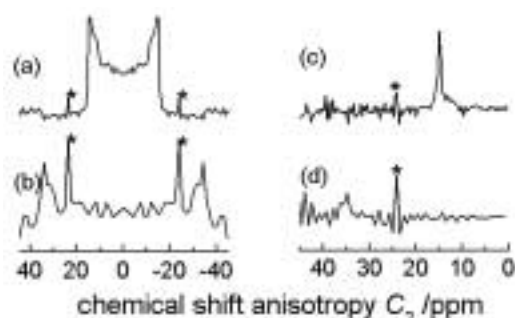
When nematic and cholesteric liquid crystals are spun around a certain axis inclined from a static magnetic field, the directors of liquid crystals can be oriented in a perpendicular direction to the spinning axis. We have reported previously that <sup>13</sup>C NMR spectra recorded under this condition can be employed to determine a molecular diffusion rate along a pitch axis of a cholesteric liquid crystal (Y. Nishiyama, *et al.*, *Mol. Phys.* **96**, 1569 (1999)). In the course of the study, we fortunately found a high-resolution two-dimensional NMR experiment, which correlates an

isotropic chemical shift and a chemical shift anisotropy of nematic liquid crystals. This technique might be also applicable to determine structures of oriented biomacromolecules in a membrane.

### V-U-1 Direct Determination of $^{13}\text{C}$ Chemical Shift Anisotropies of Liquid Crystals by Combining OMAS NMR and Rotor-Synchronous Pulses with Hankel Transformation

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The chemical shift anisotropies of liquid crystals are directly determined by a rotor-synchronous  $\pi$  pulse train under off-magic-angle spinning (OMAS). Using chemical shift anisotropies, we can determine the  $^{13}\text{C}$  NMR peak correlations between a liquid crystalline phase and an isotropic phase. These peak correlations directly enable us to assign the spectrum of a liquid crystalline phase from the assignments for an isotropic phase. When a liquid crystal with a positive (negative) magnetic susceptibility anisotropy is spun around the axis inclined from the static magnetic field by the angle  $\epsilon$  larger (smaller) than the magic angle, the directors are randomly distributed in a plane perpendicular to the spinning axis. The orientation dependence of NMR resonance frequency vanishes by the spinning averaging over a half-rotor cycle. A rotor-synchronous  $\pi$  pulse re-introduces the orientation dependence, and the resulting free induction decay (FID) is expressed by the 0th Bessel function of the first kind  $J_0(2C_2t/\pi)$ , where  $C_2$  is a coefficient related to the chemical shift anisotropy. The value of  $|C_2|$  is determined by the Hankel transformation of the FID. The sign of  $C_2$  is determined from a tilted 2D spectrum or from slices of 2D spectra recorded at two different angles  $\epsilon$ . The property of the Hankel transformation is discussed. These theoretical results were verified by  $^{13}\text{C}$  OMAS experiments with a  $\pi$  pulse train on a nematic liquid crystal of *p*-methoxybenzilidene-*p*-*n*-butylaniline (MBBA).



**Figure 1.** Comparisons between (a, b) Fourier transformed and (c, d) Hankel transformed spectra of MBBA at 302 K. The upper spectra (a, c) represent carbon-1 at 120.3 ppm and The lower spectra (b, d) represent carbon-9 at 175.1 ppm. The asterisks indicate the cycling sidebands due to the XY-8 phase cycling.