



Ph.D. Project

OPTIMAL-CONTROL APPROACH TO MULTIDIMENSIONAL SOLID-STATE NMR EXPERIMENTS OF QUADRUPOLEAR NUCLEI.

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Dramatic methodological and hardware improvement of extremely high magnetic field and mainly availability ultra-fast magic-angle spinning probes is changing the perspectives of solid-state NMR application. In the field of material research multiple studies appear characterizing silicates, boron-oxide materials, porous organic polymers, surface organometallic catalysts, and microporous metal-organic frameworks (MOFs) including our contributions focused on paramagnetic MOFs.¹ Solid-state NMR is especially relevant when diffraction methods fail due to the absence of long-range periodical arrangement.

However, **two** main limitations remain, which disable widespread application of material solid-state NMR as ubiquitous as liquid-state NMR of molecules in solution – **resolution, sensitivity**.

The resolution of NMR spectra is dictated by signal line width and their spectral separation. In solid-state the linewidth is fundamentally reduced by **Magic-Angle Spinning (MAS)**. The state-of-the art equipment, uniquely available at IOCB Prague as well, enables experiment under fast-MAS conditions leading to narrow linewidth even for direct ¹H detection. However, in a sample with a high number of signals in a narrow spectral region, the **signals overlap** even under fast-MAS conditions. In this case,

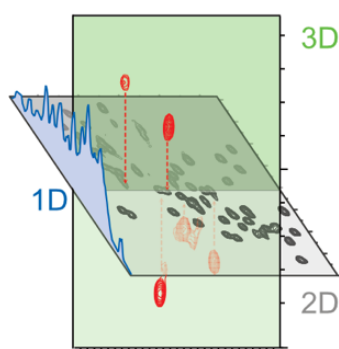


Figure 1: Comparison of 1D ¹H (blue), 2D ¹⁵N¹H (grey) and single plane from 3D ¹³CA¹⁵N¹H (green) spectra of the ¹³C,¹⁵N,²H,¹H_N-SH3 protein at 55 kHz MAS which shows an increase of spectral resolution with higher dimensionality. Based on Ref³.

resolution is restored by expanding the 1D experiment to **multidimensional**. Two-dimensional techniques have been reported many times in solid-state NMR of material (reviewed e.g. in Ref⁴). However, the expansion of experiment dimensionality to 3D or more was never reported for material samples, while it is routine in solid state NMR of proteins. (Figure 2)^{5,6} For proteins that can be isotopically labelled, multi-D experiments detect correlation between spin-1/2 nuclei like ¹⁵N and ¹³C. But these isotopes occur in low natural abundance (≤1%) and neighbouring pair of them is highly improbable. Therefore, resulting 3D experiments are extremely insensitive.

For this reason our **project focuses on high-abundant nuclei**. Depending on the targeted material, one can focus on ¹⁴N (natural abundance 99.6%), ²⁷Al (100%) or ¹¹B (80.1%). Unfortunately, all these nuclei are quadrupolar ($S > 1/2$) which makes acquisition of the solid-state NMR spectra challenging due to signal broadening and inefficient coherence transfer.^{7,8} The decrease in experiment efficiency is mostly attributed to the scaling of the dipolar interaction and the radiofrequency (rf) field in the presence of a strong quadrupolar interaction for different crystallite orientation in powder.¹³ Finding an optimal transfer pulse scheme is **mathematically very complex problem**.

We have recently addressed the question of efficient polarisation transfer in the system of $S = 1/2$ nuclei in powder and provided robust solution by numerical approach based on **optimal-control (OC)** theory.¹⁴

The numerical approach allows a **straightforward** pulse-sequence design under the conditions that are intractable analytically. Digital rf pulses are then easily added to NMR pulse sequences and typically feature higher efficiency than conventional pulses.¹⁴ Further sensitivity gain was obtained in the OC approach by overcoming the volume sensitivity of the r.f. field¹⁵ and further improvements of the multidimensional experiments.³

We therefore intend to address, for the first time, the effective coherence transfer involving quadrupolar nuclei by means of optimal control.

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