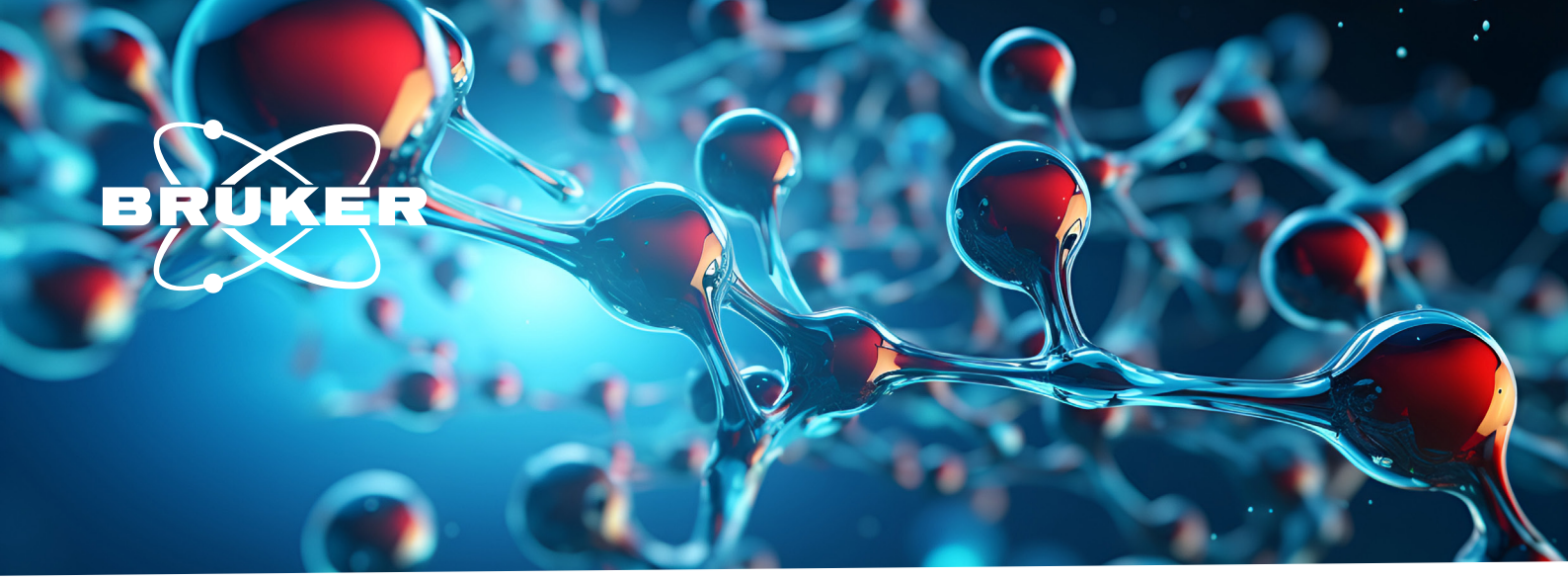

NMR

Solid-State NMR Automation

Innovation with Integrity

Abstract

In this application note, we present a method that permits the execution of most standard solid-state NMR experiments on spin ½ systems in automation. This means that a solid-state NMR experiment can be called up in TopSpin through a general parameter set and executed as soon as the sample is inserted, spun up, and the probe is tuned and matched. Following the loading of the NMR experiment's rf-parameters from the PROSOL table (analogous to what is done for high-resolution NMR experiments on liquids), the experiment can be started without extra parameter optimization or special experimental knowledge in solid-state NMR. This facilitates the execution of solid-state NMR experiments in regulated environments.

Description of the Method

The method focusses on applied radio frequency fields B_1 that are expressed and used as nutation frequencies for nucleus i, $f_{(1,i)}=1/2\pi\,|1/2\,\gamma_i\,B_{r,i}|$, which are key parameters in solid-state NMR experiments as decoupling fields or spinlock fields in cross-polarization (CP).

Strictly speaking, the term nutation frequency refers to $\omega_{1,i}=|1/2\gamma_i\,B_{rf,i}|$, with $f_{1,i}=1/2\pi\,\omega_{1,i}$. These rf-fields f_1 are often related to the mechanical sample rotation frequency about the magic angle f_{MAS}. An AU-program, embedded in the parameter set, reads the magic angle spinning (MAS) frequency automatically and writes the value of f_{MAS} to the parameter *cnst31*. The parameter, *cnst31*, is conventionally used as the MAS frequency in pulse programs. It permits that any experiment can be executed under various MAS spinning conditions following a simple standard operating procedure (SOP). The SOP consists of loading the sample, spinning it up to the desired MAS rate, loading the parameter set in TopSpin, and reading the PROSOL parameters. PROSOL parameters are read into the parameter set by either using the solvent button shown in Figure 1 or by typing *getprosol* into the command line.

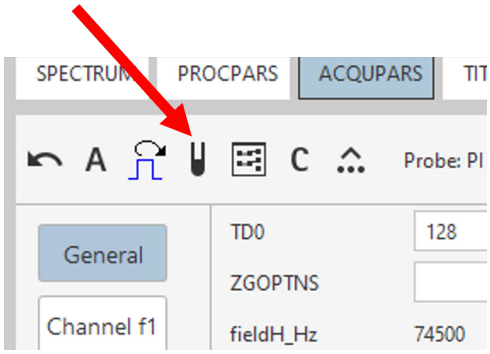

Figure 1 The solvent button in TopSpin can be used to read PROSOL parameters into the parameter set.

After tuning and matching the NMR probe to the set rf-frequencies, the experiment can be started with the command *xaua*, written into the command line of TopSpin. The command *xaua* executes an au-program which is part of the acquisition parameter set. The AU-program reads the currently set MAS frequency from the MAS controller and enters its value into *cnst31*=f_{MAS}=MASR. The parameter MASR is normally only used when the MASRSET are applied. The parameter MASR inside the acquisition status parameter-set reports the MAS frequency used when the experiment was executed. The status parameter can be looked up by using the letter s before typing the parameter name in the command line, e.g. *1s MASR* or *s MASR*.

Automatic experimentation can be implemented within IconNMR, Bruker's automation program where experiments can be loaded. IconNMR executes all necessary steps, sample loading (if a sample changer is available), tuning and matching as well as loading the proper shim file and setting the desired MAS frequency when using a CPMAS iProbe. Other CPMAS probes require manual tuning and matching after sample loading before starting the experiment in IconNMR.

Implementation in TopSpin

The pulse programs with the ideas laid out in the paper by C. Johann et al [1] were first implemented in TopSpin 4.4. These pulse programs use the concept of the nutation frequency / B_1 field and offer the possibility of correction terms in frequency units of Hz for rf-power / rf-field correction of the various pulse sequence elements in an experiment. A well setup spectrometer does not require the use of these correction terms, but they can be employed at the discretion of the spectroscopist.

The experiments consider that magic angle spinning determines many elements of solid-state NMR experiments. For example, the rf-amplitude of the spinlock pulse for the zero quantum CP matching condition. The Hartmann Hahn (HH) matching condition [2] under MAS for nuclei *i* and *s* under MAS depends on the MAS frequency [1, 2, 3],

$$f_{1,i} - f_{1,s} = nf_{MAS}.$$

For the sake of simplicity, the *s*-nucleus is any X-nucleus from ^{31}P to lower frequency nuclei while the *i*-nucleus is mostly ^{1}H and occasionally ^{19}F. Most generally, the nucleus i is the nucleus from which the magnetization is transferred, while the nucleus s is the one receiving the magnetization in a CP experiment. This is illustrated in Figure 2. The pulse program loads the specified maximum spin nutation frequency $f_{1,s}=1/2\pi\,|1/2\,\gamma_s\,B_{rf,s}\,|$, for the low gamma *i*-nucleus and calculates based on f_{MAS} with n=1 the rf-power required for $f_{1,i}=nf_{MAS}+f_{1,s}$.

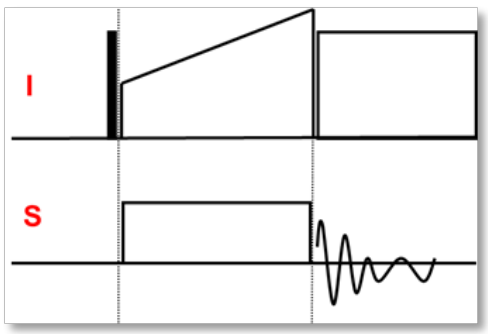

Figure 2 CPMAS experiment with nucleus i being the ^{1}H channel, typically and s any lower gamma nucleus. The contact pulse with the ramped amplitude is generally on the high gamma nucleus but can be used on the low gamma nucleus as well. Often, tangential amplitude modulated pulses are employed promising better magnetization yield [3, 4].

For calculating and setting the correct rf-power, a 10 kHz reference field is used and available in the PROSOL table [1]. The rf-fields for the spinlock pulse of the i-nucleus are taken from the PROSOL table which contains the probe specifications as well and should be setup by a Bruker engineer during installation or an NMR manager. By default, the CP pulse for the X-nucleus is a constant amplitude rf-pulse. The ^{1}H pulse uses by default a tangential amplitude modulated pulse shape [5] with an rf-field that is by f_{MAS} higher than the B_1-field of the X nucleus [1,5]. The specified maximum rf-fields for the s-spins and the maximum decoupling field for the i-spin channel as well as the reference rf-fields and rf-power values for both involved nuclei are obtained from the prosol table through the relations file, defining the relation between PROSOL table entries and the experimental parameters that are required by the pulse program.

Based on this structure, automation requires just an experiment in the form of a parameter set containing the associated pulse program for the experiment. Table 1 lists currently available parameter sets for the s-nuclei ^{31}P, ^{13}C, ^{29}Si, ^{15}N, ^{209}Pb, ^{79}Br and ^{27}Al. Other experiments can be made available by Bruker's solid-state applications team upon request.

Name	Pulse Program	Comment
1HDPMAS	onepulse	Direct Polarization experiment also called Bloch-decay.
1HSATRECT1	satrect1	Proton Detected T_1-relaxation experiment using saturation recovery.
1HSATRECT1_echo	satrect1_echo.dp	Proton Detected T_1-relaxation experiment using saturation recovery with Hahn-echo detection. Requires 8 scans.
1HHOMCOR	hH_HOMCOR.dp	Experiments for ^{1}H CS referencing and scaling factor correction in FSLG HETCOR experiments.
1HT1rho2D	hXT1rho.dp	^{1}H DP $T1_{rho}$-experiment. The parameter cnst14 is the ^{1}H spinlock field in Hz.
13CCPMAS	hX.cp	Basic ^{13}C CPMAS experiment.
13CCPMAS_LPDEC	hX.cp	^{13}C CPMAS experiment with low-rf-field decoupling and extended acquisition time beyond 50ms. The low power decoupling is by default ¼ of MAS frequency. Standard parameter set for adamantane shimming and referencing experiments.
13CCPNQS	hXnqs.cp	^{13}C editing experiment for full suppression of non-quaternary carbons (also called dipolar dephasing, vary d20 and adjust the echo delay if necessary.
13CCPPI	hXcppi.cp	^{13}C multiplicity editing experiment. Vary p16 for optimal CH2-negative intensity, CH groups. Optional: set p15 38 us and p16 to 45 us permits detecting CH_2 only spectra.
13CCPTOSS	hXtoss.cp	^{13}C Total Sideband suppression for slower MAS rates. Make sure, delays stay positive, through adjustment of MASR or p2 do not collide, else spin slower or increase rf-power for a shorter p2.
13CCPTOSSNQS	hXtoss_nqs.cp	^{13}C experiment with dipolar dephasing and TOSS. Optimal dephasing time removes CH and CH_2 resonances.
13CDPMAS	hX.dp	^{13}C direct polarization experiment with ^{1}H decoupling.
13CDPMAS_LPDEC	hX.dp	^{13}C direct polarization experiment with ^{1}H low power decoupling at ¼ of the MAS frequency and with longer acquisition time.
13CHETCOR2D	hXHETCOR.cp	^{13}C-1H correlation experiment using FSLG homonuclear decoupling. The sampling rate in t1 is determined by the parameter L3.
13CT12D	hXT12D.cp	^{13}C CP based T_1-experiment using the Denis Torchia trick leading to, $M_\infty=0$, which permits faster experimentation and easier fitting the relaxation to an exponential decay.
15NCPMAS	hX.cp	^{15}N CPMAS experiment with ^{1}H high power decoupling.
15NDPMAS	hX.dp	^{15}N DPMAS experiment with ^{1}H high power decoupling.
27AlDPMAS	hX.dp	^{27}Al DPMAS experiment.
29SiCPMAS	hX.cp	^{29}Si CPMAS experiment with ^{1}H high power decoupling.
29SiDPMAS	hX.dp	^{29}Si DPMAS experiment with ^{1}H high power decoupling.

Name	Pulse Program	Comment
31PCPMAS	hX.cp	^{31}P CPMAS experiment with ^{1}H high power decoupling.
31PDPMAS	hX.dp	^{31}P DPMAS experiment with ^{1}H high power decoupling.
31PSATRECT1	satrect1	^{31}P DPMAS T_1-saturation recovery experiment with ^{1}H high power decoupling.
207Pb	onepulse	^{207}Pb DPMAS experiment.
19FDPMAS	hX.dp	^{19}F DPMAS experiment.
19FSATRECT1_echo	satrect1_echo.dp	^{19}F DPMAS T_1-saturation recovery experiment.

Table 1 Solid-state NMR Experiments which make use of the method described in this application note. The extension *.dp stands for direct polarization while *.cp stands for cross polarization experiment.

Practical Examples

Figures 3 and 4 show examples from automatic experiment runs. The only optimization required is the optimization of the recycle delay D1 by measuring the ^{1}H T_1-relaxation using either 1HSATRECT1 or SATRECT1_echo. The latter uses a Hahn-echo experiment for the ^{1}H detection which can reduce the 1H background of a probe. The first experiment uses 1 scan and is quick, while the second requires 8 scans.

The recycle delay D1 is determined by multiplying T_1 with a factor k, $D_1 = kT_1, k \geq 1.4$. The factor depends on the type of the experiment.

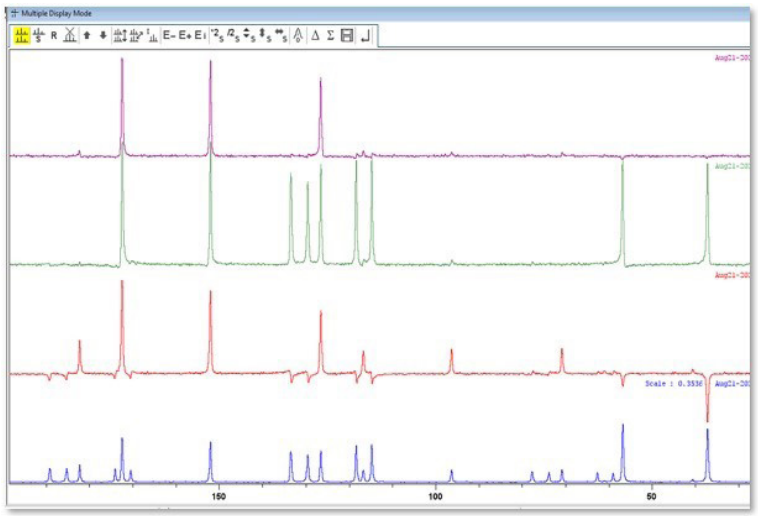

Figure 3 ^{13}C CPMAS project on tyrosine with an automation run at 7 kHz MAS using IconNMR. CPMAS is shown in blue, CPPI multiplicity editing [2] in red, CPTOSS in green and TOSS NQS in purple.

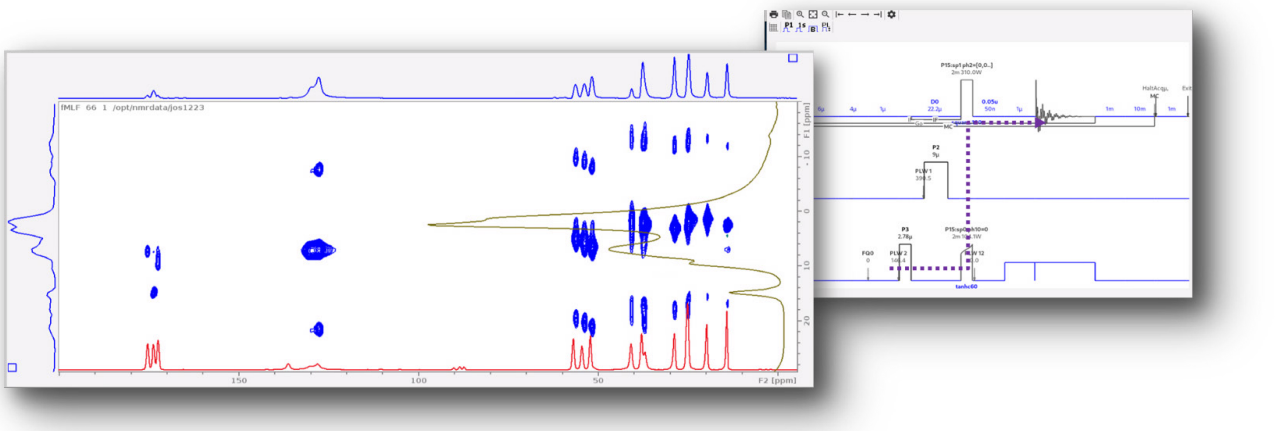

Figure 4 ^{13}C HETCOR experiment on fMLF tripeptide run in full automation [5]

Solid-State NMR Experiments with IconNMR

All experiments above can be easily used with or without a sample changer in IconNMR. The IconNMR setting is straightforward and permits acquiring data for projects on one or more samples [6]. After running the ^{1}H T_1-experiment, the experiments can be queued up in IconNMR setting D1 appropriately and choosing the desired MAS rate, which may be different for the different experiments. IconNMR will change and adjust the MAS rate as desired and run the queued experiments in sequence. The spectra in Figures 3 and 4 were obtained using IconNMR.

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