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^{19}F-decoupling of half-integer spin quadrupolar nuclei in solid-state NMR: Application of frequency-swept decoupling methods

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ABSTRACT

In solid-state NMR studies of minerals and ion conductors, quadrupolar nuclei like ^{7}Li, ^{23}Na or ^{133}Cs are frequently situated in close proximity to fluorine, so that application of ^{19}F decoupling is beneficial for spectral resolution. Here, we compare the decoupling efficiency of various multi-pulse decoupling sequences by acquiring ^{19}F-decoupled ^{23}Na-NMR spectra of cryolite (Na_3AlF_6). Whereas the MAS spectrum is only marginally affected by application of ^{19}F decoupling, the 3Q-filtered ^{23}Na signal is very sensitive to it, as the de-phasing caused by the dipolar interaction between sodium and fluorine is three-fold magnified. Experimentally, we find that at moderate MAS speeds, the decoupling efficiencies of the frequency-swept decoupling schemes SW$_f$-TPPM and SW$_f$-SPINAL are significantly better than the conventional TPPM and SPINAL sequences. The frequency-swept sequences are therefore the methods of choice for efficient decoupling of quadrupolar nuclei with half-integer spin from fluorine.

1. Introduction

In solid-state NMR of systems with dipolar couplings, sensitivity and resolution of the spectra may be improved by magic-angle spinning (MAS), and/or by application of spin decoupling using RF irradiation [1,2]. In the context of materials science, most NMR-observable nuclei of interest have a half-integer spin $I > 1/2$, such as ^{7}Li, ^{23}Na ($I = 3/2$), or ^{25}Mg, ^{27}Al ($I = 5/2$), which possess a quadrupole moment [3,4]. Solid-state NMR characterisation of materials containing quadrupolar nuclei is often restricted to observing the position and shape of the central-transition (CT) resonance ($m = -1/2 \rightarrow 1/2$), under either static or MAS conditions. The CT line is affected by the second-order contribution of the quadrupolar interaction (which cannot be completely averaged by MAS), the spatial dependence of which results in a characteristic powder pattern. If such a characteristic 'second-order shape' of the CT resonance can be observed, the NMR interaction parameters may be determined from one-dimensional spectra [3,4], and can be correlated to structure and properties of the compounds under investigation. A more precise determination is possible by using two-dimensional methods such as MQMAS spectroscopy [5,6], which add a high-resolution dimension.

Obviously, NMR spectra of quadrupolar nuclei also benefit from application of heteronuclear spin decoupling [7–20]. Interestingly, this benefit is magnified when using decoupling for acquisition of MQMAS spectra, since MQ coherences with coherence order p will undergo p-fold de-phasing during the MQ evolution period. This was realised soon after the introduction of the MQMAS technique [10–13]. Theoretical descriptions of this effect under MAS were put forward by Duer [11] and Friedrich et al. [12] using spherical tensor notation. For a static case, the p-fold de-phasing can also be understood in a straightforward manner by evaluating the influence of the dipolar interaction on the energy levels of the half-integer spin nucleus, as shown in the Appendix of this paper. Since NMR signals collected via a coherence of order p are p-fold more sensitive to the effect of heteronuclear decoupling, they constitute a good proving ground for decoupling sequences. In solid-state NMR, multi-pulse decoupling schemes such as TPPM [21] and SPINAL [22] have been shown to be much superior to continuous wave (CW) decoupling, and in a study from 1998, this superiority of TPPM was also demonstrated in the context of decoupling MQMAS spectra [13]. Recently, frequency-swept versions of TPPM and SPINAL were suggested, namely SW$_f$-TPPM [23–26] and SW$_f$-SPINAL [27]. Both were found to have improved decoupling performance and better robustness towards NMR parameter changes when compared to the original sequences. The enhanced efficiency of SW$_f$-TPPM for decoupling of protons from quadrupolar nuclei has also been demonstrated [18–20]. Here, we investigate the performance of SW$_f$-TPPM and SW$_f$-SPINAL for decoupling ^{19}F while observing a

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quadrupolar nucleus, using the 3Q-filtered signal of ^{23}Na as a benchmark. The necessity for efficient decoupling of ^{19}F occurs frequently in solid-state NMR, as fluorine is present in many important materials like polymers, minerals, and ion conductors. In many ion conductors, fluorine is found in close vicinity of quadrupolar nuclei like ^{7}Li, ^{23}Na or ^{133}Cs [28–31], which lends practical relevance to our study. It is known that ^{19}F-decoupling is more challenging than proton decoupling because fluorine possesses a much larger chemical shielding anisotropy (CSA) and a wider dispersion of isotropic chemical shifts. For a spin-1/2 nucleus (^{13}C) in a rigid organic solid, we have recently shown that the large chemical shift interaction of ^{19}F does indeed compromise the decoupling performance of multi-pulse sequences [32]. In particular, numerical simulation showed that the decoupling efficiency drops with increasing magnitude of the CSA, which may be partly attributed to the existence of second-order cross-terms between the chemical shift and heteronuclear dipolar coupling tensors [33,34]. However, the relative performance hierarchy of the investigated multi-pulse sequences remained unaffected by the CSA magnitude, with the frequency-swept sequences being the most efficient [32]. As detailed below, we also find SW$_f$-TPPM and SW$_f$-SPINAL performing best for decoupling ^{19}F from our test nucleus ^{23}Na. Since we explored only the regime of moderate sample spinning frequencies, the decoupling efficiencies of sequences like XiX [35] and PISSARRO [36] have not been evaluated, as they are designed to work at high MAS speeds.

2. Experimental

A polycrystalline sample of cryolite (Na_3AlF_6) was obtained from Fluka AG and used without further purification. The ^{23}Na NMR spectra of Na_3AlF_6 were acquired on Bruker AVANCE-III 400 spectrometer, at a Larmor frequency of $\nu_0(^{23}\mathrm{Na}) = 105.843$ MHz, using a 4 mm MAS probe at spinning frequencies of 10–12 kHz. The ^{23}Na NMR chemical shifts were referenced to a dilute aqueous sodium chloride (NaCl) solution, with the ^{23}Na signal at 0 ppm. For the acquisition of full 3QMAS spectra, a split-t_1-whole echo sequence [37,38] with a 48-step phase cycle was used. (For ^{23}Na with $I = 3/2$, a 48-step cycle was sufficient to obtain an artefact-free spectrum, although the recommended phase cycle for a split-t_1-whole echo 3QMAS contains 96 steps [6].) Three hundred and sixty transients were recorded for each t_1 increment of 25 μs, with 128 increments in the F_1 dimension. The 'classical' two-pulse scheme for 3Q excitation and conversion, P_H^{exc}–P_H^{con}, was used with a short 3Q evolution delay of $t_1 = 3$ μs to optimise the respective pulse durations, with the best values being $P_H^{exc} = 3.0$ μs and $P_H^{con} = 1.5$ μs with a RF nutation frequency of 111 kHz. The selective split-t_1-echo pulse was 20 μs with a nutation frequency of 28 kHz. The isotropic (F_1) dimension of the MQ-MAS experiments have been labelled according to the convention which scales the evolution period by $(1+k)$. For a 3Q-MAS experiment of ^{23}Na ($I = 3/2$) nucleus, the F_1 scaling factor is 16/9, with the k value being 7/9 [39].

2.1. Optimisation of ^{19}F decoupling sequences

The ^{19}F decoupling for ^{23}Na MAS NMR and 3Q-MAS experiments was done at a Larmor frequency of $\nu_0(^{19}\mathrm{F}) = 376.433$ MHz, with an RF strength of $\nu_1 \approx 50$ kHz. The 3QMAS two-pulse sequence described above was also used to assess the effect of various decoupling schemes by recording ^{23}Na 3Q-filtered spectra. This means looking only at the first t_1 slice of a full 3QMAS, to be able to compare decoupling efficiency quickly, as has been described in a previous publication [20]. This may be used to optimise the parameters governing the decoupling sequences, such as pulse durations, phase angles and sweep profiles by searching for the maximum intensity of the 3Q-filtered ^{23}Na signal. In Fig. 2, the change of decoupling efficiency in dependence of the phase angle ϕ is plotted for the TPPM sequence. It can be seen that the trend of intensities observed from the 3Q-filtered MAS spectra (F_2 traces) is very similar to that obtained from recording and comparing the F_1 traces of full 3QMAS spectra. Care needs to be taken that the F_2 traces shown in Fig. 2a possess a sufficient signal-to-noise ratio to evaluate the influence of parameter change, which in practice means acquisition of more transients than one would use for a single slice in the full 3QMAS. For Fig. 2a, 2400 transients with a recycle delay of 2 s were acquired. This is however still much faster than the 360×128 transients required to obtain the F_1 slices shown in Fig. 2b.

Using a combination of 3Q-filtered F_2 slices and acquisition of full 3QMAS spectra to compare F_1 slices, the following parameters were found to perform best for the respective sequences (pulse durations were identical for all sequences with $\tau_p = 8$ μs):

- TPPM: phase angle $\phi = 7.5^\circ$.
- SPINAL-64: phase angle $\phi = 7.5^\circ$, phase increments $\alpha = 5^\circ$, $\beta = 10^\circ$.
- SW$_f$-TPPM: phase angle $\phi = 17.5^\circ$; 11 pulse pairs with a sweep window from 0.78 to 1.22, using a linear sweep profile [26].
- SW$_f$-SPINAL: phase angle $\phi = 12.5^\circ$; phase increments $\alpha = 5^\circ$, $\beta = 10^\circ$; sweep over 16 pulse pairs (hence SW$_f$(32)-SPINAL-32 [27]), with a linear sweep from 0.90 to 1.10.

3. Results and discussion

In Fig. 1, the ^{23}Na-NMR spectrum of cryolite (Na_3AlF_6) at 12 kHz MAS rate is shown with and without application of ^{19}F decoupling. The small impurity signals appearing in the ^{23}Na spectra are likely due to various sodium fluoroaluminate species. These are known to form during the preparation of synthetic cryolite depending on the reaction conditions like humidity, temperature, etc., and have been investigated in detail by Scholz et al. [40]. As can be seen from Fig. 1b, the ^{19}F decoupled spectrum (at a comparatively small decoupling field strength of $\nu_1 \approx 50$ kHz) exhibits better resolution than the non-decoupled one. From the atomic coordinates determined by single-crystal X-ray diffraction [41], we can calculate that the largest Na–F dipolar coupling present in cryolite is about 2.7 kHz. However, even at 12 kHz MAS the effects of dipolar coupling do not vanish completely, as cross-terms between dipolar, ^{23}Na quadrupolar

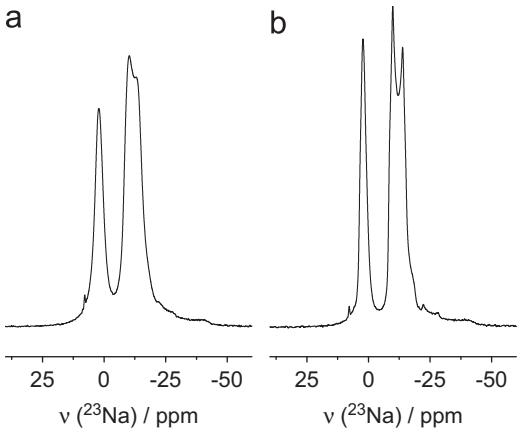

Fig. 1. The ^{23}Na MAS NMR spectrum of cryolite (a) without and (b) with ^{19}F decoupling at 12 kHz MAS frequency in a 9.4 T magnetic field. The decoupling method employed was SW$_f$-SPINAL.