

A very sensitive high-resolution NMR method for quadrupolar nuclei: SPAM-DQF-STMAS

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We show that by combining the intrinsically larger (with respect to MQMAS) efficiency of Double-Quantum Filtered Satellite-Transition MAS (DQF-STMAS), with the large S/N gain of the Soft-Pulse Added Mixing (SPAM) concept, a new very sensitive high-resolution solid-state NMR method can be obtained for semi-integer quadrupolar nuclei.

Nuclear magnetic resonance (NMR) is one of the most powerful tool available to the community of researchers in various areas of physics, chemistry, materials science, biology and medicine. NMR's ability to probe the structure of materials strongly depends upon the availability of high-resolution spectra, which serve as fingerprints of the physico-chemical surroundings of the studied nuclei. Initially, such spectra could only be obtained in liquids. The resolution gap between liquid and solid-state NMR began to decrease in the 1960s with the introduction of RF decoupling, and magic angle spinning (MAS),¹ which allowed for increasingly precise measurements of isotropic chemical shifts (δ_{cs}) of spin $S = 1/2$ nuclei.

Until recently, however, these techniques could not overcome the line broadening in NMR spectra of the quadrupolar nuclei with spin $S > 1/2$. This broadening arises from the coupling of the non-spherical charge distribution of such nuclei with the electric field gradients created by the surrounding electrons. The quadrupolar broadening is 'more anisotropic' than the first-order interactions (shielding and dipolar coupling), in the sense that it contains higher-order orientational terms of significant magnitudes. For half-integer spins, the first-order quadrupolar effect on the satellite transition (ST) frequencies ($m - 1 \leftrightarrow m, m \neq 1/2$) is of the order of $C_Q = e^2qQ$. Thus, in a powdered sample, the NMR spectrum is spread over a wide frequency range. However, the central transition (CT: $-1/2 \leftrightarrow 1/2$) is not affected to first-order and only second-order terms influence its frequency. Therefore, the powder CT line-width is typically 10^2 to 10^3 times smaller than C_Q , and this transition yields a narrower and more intense spectrum, which is the subject of most studies on half-integer quadrupolar nuclei. In the last two decades most experiments utilized the line-narrowing effect of MAS, which eliminates the first-order broadening completely and reduces the second-order quadrupolar contribution to the CT line-width by a factor of approximately three. Recently, it has been demonstrated that the remaining CT MAS-broadening can be cancelled by changing the coherence state of the observed spins.² This experiment, referred to as Multiple Quantum MAS (MQMAS), is a 2D method, which correlates the phase evolutions of the MQ (t_1) and single quantum CT (t_2)

coherences and allows for observation of a purely isotropic echo. Very recently, another technique referred to as Satellite Transition MAS (STMAS) has been proposed.³

This technique provides isotropic spectra by correlating the evolution of single quantum inner-STs ($\pm 3/2, \pm 1/2$) in t_1 with that of the CT during t_2 . For all crystallite orientations, both methods refocus the second-order quadrupole dephasings along a unique axis with slope $R(S)$. This refocusing allows obtaining 2D frequency spectra from which the indirect dimension becomes, after shearing, an isotropic dimension (δ_{iso}), and the second dimension (δ_2) is the classical MAS one.

In STMAS (and MQMAS), the most frequently used sequences are composed of three pulses: two hard-pulses (HP₁ for the creation of inner-STs and then, after t_1 , HP₂ for their conversion), followed by one soft-pulse (SP).

In order to enhance the sensitivity of MQMAS, an improvement that concerns the ensemble HP₂-SP has been very recently proposed.^{4,5} Up to now, in all MQMAS sequences, a single coherence quantum level is selected in between HP₂ and SP: 0Q in z -filter⁶ and +1Q in full-echo^{7,8} experiments. The proposed idea, called SPAM (Soft Pulse Added Mixing), is to use in a constructive way all quantum levels in between HP₂ and SP, based on a complete alias of coherence transfer pathways. It has recently been shown that this modification of the basic sequence allows doubling the echo and anti-echo signals in MQMAS.^{4,5} In SPAM based experiments, phases related to HP₂ and SP are set to $\pm x$ in order to select all coherence levels in between these two pulses. These pulse phases have same or opposite signs according to whether the global transfer for these two pulses is in between quantum levels of opposite or identical signs, respectively. SPAM pulse sequences require the acquisition of the echo and anti-echo pathways, separately, in opposition to z -filter methods,⁶ for which echo and anti-echo are recorded simultaneously. This thus leads to the echo/anti-echo method and data treatment in which the real part of the final spectrum is in pure absorption mode.⁹ However, for a fixed experimental time, the signal can be increased by recording only a few FIDs for the anti-echo pathway and zero-filling all other FIDs to decrease the noise. Indeed, due to the negative $-R(S)$, slope of the anti-echo signal in the time domain, the contribution of the anti-echo pathway to the signal becomes negligible, if not non-existent, after a few t_1 steps. Globally, it has been shown that the SPAM echo/anti-echo method allows gaining a factor of *ca.* 3 for the signal to noise ratio with respect to that obtained with the original z -filter experiment.⁵

The aim of this communication is to show that the intrinsically larger (with respect to MQMAS) efficiency that can be obtained with STMAS methods, can be combined with the large S/N gain

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that can be obtained by using the SPAM concept. We demonstrate this by recording an ^{17}O ($S = 5/2$) SPAM-STMAS 2D spectrum of a glass compound: $30\text{Nb}_2\text{O}_5\text{-}70\text{NaPO}_3$, which belongs to the binary system: $x\text{Nb}_2\text{O}_5\text{-(}100 - x\text{)NaPO}_3$. ^{31}P MAS spectra have shown that for increasing x molar fraction, a depolymerisation of the phosphate glass network occurs. Moreover, the fitting of these spectra have indicated the presence of Nb–O–Nb sites by comparing the fraction of experimental Q^n sites with calculated values. The presence of these sites were confirmed by ^{93}Nb NMR results.¹⁰ Due to its large chemical shift range (≈ 500 ppm), ^{17}O NMR is expected to enable the differentiation of the different oxygen environments present in these glasses. We have chosen to study here the glass with $x = 30$ molar fraction in Nb_2O_5 . Indeed, this fraction is close to the limit of crystallisation that occurs for $x > 40$, and hence it is well adapted to observe oxygen sites with niobium as neighbours. The main objective of this communication is to show that, even with a standard field (9.4 T) NMR spectrometer, different ^{17}O sites can easily be detected with this moderate ($x = 30$) Nb_2O_5 fraction, using SPAM-STMAS. The glass was prepared by heating of ^{17}O enriched NaPO_3 and Nb_2O_5 in a platinum crucible at 1300°C for 20 min. NaPO_3 was enriched according to the procedure describe in ref. 11 and Nb_2O_5 by hydrolysis of NbCl_5 with ^{17}O -enriched H_2O . No weight loss was detected during the melting, so the glass composition is considered to be close to the batch composition. We estimate the ^{17}O enrichment to be *ca.* 30%.

In order to cancel all unwanted signals (CT \rightarrow CT and outer-STs \rightarrow CT), we used the recent DQF-STMAS method,¹² which includes a CT-selective double-quantum filter π pulse before HP_2 . The DQF-STMAS pulse sequence in its z -filter version as well as its coherence transfer pathway are described in Fig. 1(a) and (b). The coherence transfer pathway of the SPAM version of the DQF-STMAS is given in Fig. 1(c).

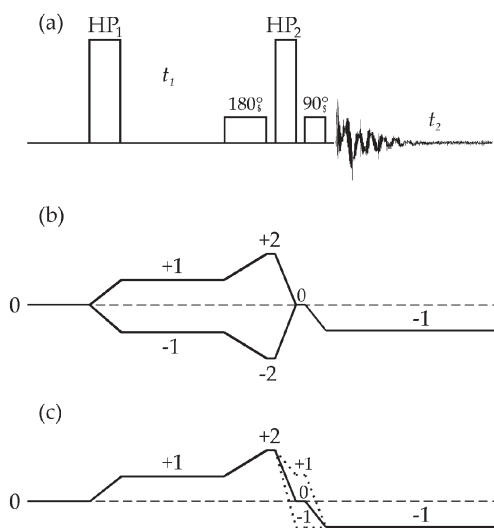


Fig. 1 DQF-STMAS: (a) pulse sequence; (b) z -filter: coherence transfer pathway;¹² (c) SPAM version: coherence transfer pathway for echo ($S > 3/2$). Phases of the second hard and soft pulses were fixed to 0° in order to add signals issuing from all pathways.^{4,5} The delay between these two pulses must be as short as possible to avoid any dephasing occurring on non-0Q levels. Level $-1Q$ must be selected during t_1 for anti-echo ($S > 3/2$) or echo ($S = 3/2$) signals.

In order to cancel first-order quadrupolar dephasings occurring during t_1 , the rotor-axis must be exactly adjusted at the magic-angle, and t_1 must be perfectly rotor-synchronized. Magic angle settings usually rely on optimizing the amplitude and number of spinning ST sidebands in a single pulse experiment of a solid compound with a small quadrupole interaction. However, STMAS experiments require a much more precise magic angle setting that can be done by a rapid acquisition of 2D DQF-STMAS spectra on a model compound. Other parameters (automatic insert/eject of the sample, stability of the spinning, ...) are important to consider prior to running a DQF-STMAS spectrum and they are extensively described in ref. 13. In the present communication, these considerations are much less critical due to the fact that the remaining miss-adjustment will be overshadowed by the large distribution often observed on such spectra of amorphous samples, such glasses. In order to cancel the first-order quadrupole interaction, the evolution time t_1 must be rotor-synchronized to pick the top of ST rotational echoes. As this interaction is very large, this synchronization must be perfect, and the definition of t_1 time must take into account the two hard-pulse lengths. Another important consequence of this perfect rotor-synchronization is that the spinning speed must be perfectly stable. One way to improve the speed stability is by using several tanks after the air compressor, several evenly spaced marks on the rotor, and a good speed controller. By doing so, it has been shown that the spinning rate can indeed be controlled within ± 0.1 Hz.^{14,15} We have used a Bruker AVANCE-400 console and 4 mm diameter rotors. For the SPAM-3QMAS spectrum, the spinning speed was 10 kHz. For the SPAM-DQF-STMAS spectrum, we have used a special MAS probe-head with a sturdy goniometrical adjustment of the magic angle. The spinning speed was adjusted at 12000 ± 2 Hz with a classical Bruker speed controller. However, we did not observe any t_1 noise, because of the small S/N ratio. RF field amplitudes were 150 and 10 kHz for hard and soft pulses, respectively.

We have recorded a classical z -filter 3QMAS experiment,⁶ to observe a single resonance (PONA) after a total experimental time of 48 h (not shown). With the SPAM-3QMAS method,⁵ we managed to distinguish a second oxygen site (PONb) after the same experimental time (Fig. 2(a)). However, the isotropic spectral

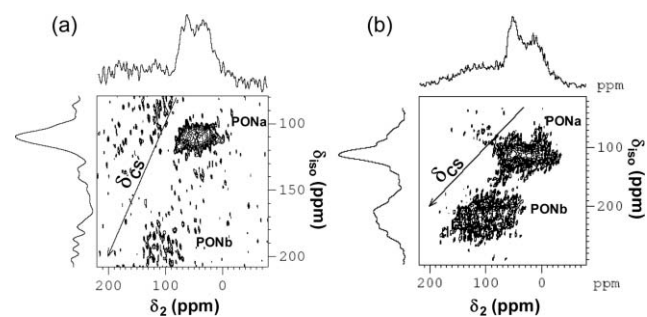


Fig. 2 2D ^{17}O sheared spectra of $30\text{Nb}_2\text{O}_5\text{-}70\text{NaPO}_3$: (a) SPAM-3QMAS, and (b) SPAM-DQF-STMAS. The spectra were recorded with 32 echo t_1 slices, but no anti-echo, a recycling delay of 1 s, in 48 h (a) and 17 h (b). For each echo t_1 slice, 5400 FIDs were accumulated in (a) and 1920 in (b). We have verified that introducing anti-echo t_1 slices did not change the spectrum.

width was too small and a folding of PONb resonances was observed along δ_{iso} .

Things were completely different when using SPAM-DQF-STMAS, and two different signals with good S/N ratio were observed after only 17 h of acquisition (Fig. 2(b)). Moreover, due to a doubling of isotropic spectral width with respect to 3QMAS,¹⁶ no folding of the resonances along δ_{iso} occurred (Fig. 2(b)).

The two observable sites ($\delta_{\text{iso}} \approx 215$ ppm, $\delta_2 \approx 100$ ppm, $P_Q \approx 5.9$ MHz, $\delta_{\text{cs}} \approx 172$ ppm) and ($\delta_{\text{iso}} \approx 110$ ppm, $\delta_2 \approx 30$ ppm, $P_Q \approx 4.9$ MHz, $\delta_{\text{cs}} \approx 80$ ppm) can be attributed to oxygen atoms with Nb and Na neighbours,¹¹ respectively.

In conclusion, we have shown that ¹⁷O SPAM-DQF-STMAS NMR is an efficient method to observe the oxygen sites. This sequence will enable the identification of different oxygen sites in the $x\text{Nb}_2\text{O}_5-(100-x)\text{NaPO}_3$ glasses with smaller Nb₂O₅ concentrations, which are more difficult to detect. The software used for SPAM acquisition and treatment (including shearing process and unified ppm scaling¹⁶) will very soon be available on the Bruker web-site.

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