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^{29}Si and ^{17}O (Q)CPMG-MAS solid-state NMR experiments as an optimum approach for half-integer nuclei having long T_1 relaxation times

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Abstract

A significantly reduced experiment time for half-integer nuclei with long T_1 relaxation times has been demonstrated by ^{29}Si CPMG-MAS or ^{17}O QCPMG-MAS experiments on α -cristobalite, a radiation damaged Zircon and ^{17}O enriched α -quartz, respectively. For ^{29}Si up to 37 h were saved compared to the MAS experiment using longer cycle periods (up to 3600 s) but fewer scans. The spectrum reconstructed from the echoes provides similar spectral information as the MAS spectrum. In the ^{17}O spectrum increased sensitivity facilitated determination of CSA in α -quartz at 9.4 T and points towards a method to obtain natural abundance ^{17}O spectra of non-cubic oxides. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclei having long longitudinal relaxation times (T_1) represent a major obstacle for every NMR spectroscopist. Unfortunately some of the very informative nuclei in minerals such as ^{17}O , ^{29}Si , and ^{31}P belong to this group of NMR active isotopes. The current method to acquire spectra of these nuclei is by single-pulse magic-angle-spinning (MAS) using a small flip-angle and

thereby a shorter recycle delay. For synthetic samples this is often combined with addition of small amounts of paramagnetic impurities to reduce the relaxation time but when dealing with rare and/or expensive samples the latter approach may not be an option. The traditional method of accumulating ^{29}Si spectra, in particular, generally requires an overnight run to obtain sufficient signal to noise. In addition, unless special precautions are taken, the equilibrium magnetization may not be established even with recycle delays of hundreds of seconds.

In this work the Carr–Purcell–Meiboom–Gill [1] MAS (CPMG-MAS) or the Quadrupolar CPMG-MAS (QCPMG-MAS) experiment [2,3] will be shown to be a robust method for dealing with such compounds. The presence of a long T_1

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in inorganic oxides and minerals is generally accompanied by a long transverse relaxation time (T_2). Pulse train techniques take advantage of the latter to refocus magnetization, and record a magnetic resonance signal many times, thus increasing the total signal acquired for any particular scan. The scan can then be repeated at much longer intervals thereby increasing the likelihood of establishing the equilibrium magnetization and the accuracy of the experimental spectrum. In the cases we have studied we have seen no differential T_1 relaxation where this aspect of the experiment would be important. However, this may be important in other samples. Another advantage of this method of signal accumulation is for in situ kinetic experiments, which have been almost impossible for ^{29}Si in natural abundance because of long acquisition times. Static QCPMG experiments on ^2H in DMS- d_6 have been shown to provide sensitivity gains of about an order of magnitude compared to quadrupole echo (QE) [4,5] experiments as well as introducing the spin-echo sidebands whose lineshape is very sensitive to dynamics [6]. Therefore it is conceivable that pulse train techniques could now provide a method for examining in situ the recovery of radiation damage in ceramics or glasses at repository temperatures (200–300 °C).

Previously the (Q)CPMG-MAS method have been demonstrated on half-integer quadrupolar nuclei with the benefit of gaining at least an order of magnitude in sensitivity compared to the standard spin-echo experiment. The applicability for nuclei with long relaxation times have partly been touched on before in relation to static QCPMG experiments on ^{39}K in K_2MoO_4 where it was shown that the intensity of the echoes during the pulse train was only reduced by 30% over an acquisition period of 60 ms using a recycle delay of 16 s [7]. Furthermore the static method has proven valuable for acquiring spectra at very low temperatures (down to 25 K) which extends the relaxation time substantially [8,9].

At present three samples will be analyzed, ^{17}O enriched α -quartz (SiO_2) by ^{17}O QCPMG-MAS as well as α -cristobalite (SiO_2) and a radiation damaged Zircon (ZrSiO_4) sample by natural abundance ^{29}Si CPMG-MAS NMR.

2. Experimental

The experiments are performed on a Chemagnetics Infinity 400 spectrometer using double resonance Chemagnetics TR3 probes equipped with either 4 or 7.5 mm (o.d.) Zirconia rotors. For ^{17}O the Larmor frequency was 54.23 MHz and an rf-field strength of 27.7 kHz (4 mm) was applied. For ^{29}Si the Larmor frequency was 79.48 MHz and the rf-field strengths were 83.3 (4 mm) or 50.0 kHz (7.5 mm), respectively.

Samples of α -cristobalite and α -quartz are prepared by reacting SiCl_4 with H_2^{17}O (47% isotopically enriched) and then annealing at high temperature under N_2 atmosphere to produce crystalline phases. The materials are hereafter carefully grinded to obtain a powder sample and packed in 4 mm rotors. The radiation damaged Zircon (Cam26) is a 152 mg piece of Zircon that has been exposed to an α dose of 2.9×10^{18} α/g . The Zircon has been packed in the rotor (7.5 mm) with a slurry of PbNO_3 in order to obtain an evenly distributed density in the sample chamber [15].

For an overview of the (Q)CPMG-MAS pulse sequence this may be depicted as

$$\left(\frac{\pi}{2}\right)_S - \tau_1 - (\pi)_S - \tau_2 - \text{Acq}\left(\frac{\tau_a}{2}\right) - [\tau_3 - (\pi)_S - \tau_4 - \text{Acq}(\tau_a)]^M - \text{Acq}(\tau_d),$$

where $(\pi/2)_S$ denotes a $\pi/2$ pulse selective for the $(1/2, -1/2)$ transition. That is, the nominal pulse length has to be divided by $(I + 1/2)$. τ_1 and τ_2 usually equals a rotor period (τ_r), $\text{Acq}(\tau_j)$ denotes acquisition in a period τ_j , M is the number of repetitions of the refocusing and rotor synchronization is obtained by setting $2N \cdot \tau_r = \tau_3 + (\pi)_S + \tau_4 + \tau_a$, where N is an integer. Other parameters are adjusted as described previously [2,3]. Fourier transformation of a FID acquired this way results in splitting of the resonance lines into spin-echo sidebands separated by $1/\tau_a$. Numerical simulations and iterative fitting of the quadrupolar and chemical shift tensors along with their relative orientation were performed on a 550 MHz PC Pentium III using the theoretical approach and a modified version of the software described elsewhere [3].

3. Results and discussion

In Fig. 1 the experimental (Fig. 1b) and calculated (Figs. 1a,c) QCPMG-MAS spectra of α -quartz are displayed. The experimental spectrum is acquired using a recycle delay of 20 min and 40 scans (total acquisition time of 13.33 h). An approximately 7 kHz wide centerband along with separate first-order spinning sidebands are observed.

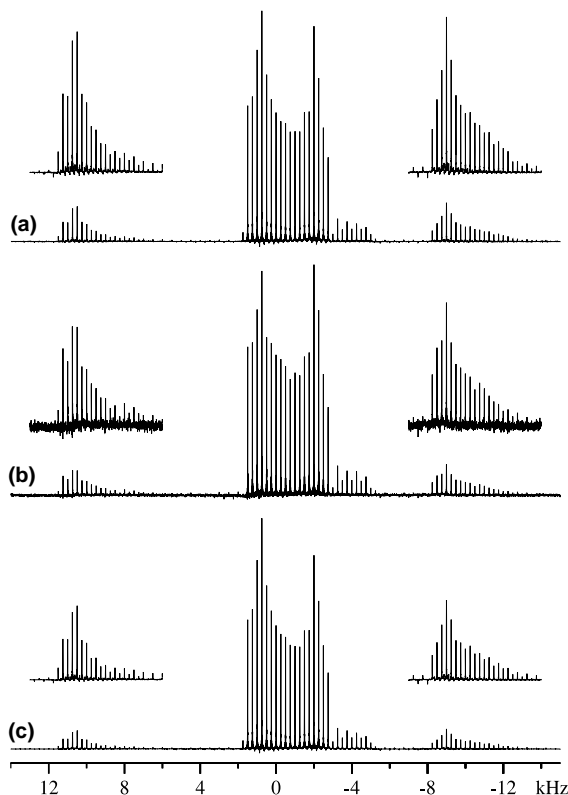


Fig. 1. Experimental (b) and calculated (a,c) ^{17}O (54.23 MHz) QCPMG-MAS spectra of α -quartz. The experimental spectrum is acquired using $(\pi/2)_S = 3.0 \mu\text{s}$, $\tau_1 = \tau_2 = 101.85 \mu\text{s}$, $\tau_3 = \tau_4 = 34.00 \mu\text{s}$, $\tau_a = 4.0 \text{ ms}$, $M = 30$, $\tau_d = 1.6 \text{ ms}$ using a dwell time of $8.0 \mu\text{s}$ and employing a spin-rate of 9818 Hz. 40 scans are acquired with a recycle delay of 1200 s. The calculated spectrum in (a) employs the following parameters: $C_Q = 5.21 \text{ MHz}$, $\eta_Q = 0.19$ and $\delta_{\text{iso}} = 43.0 \text{ ppm}$, $\delta_\sigma = 52 \text{ ppm}$, $\eta_\sigma = 0.62$ and $\Omega_{\text{PC}}^{\text{PC}} = (91, 0, 179)^\circ$. For the calculation in (c) the contribution from the CSA is omitted. The experimental spectrum is apodized by Lorentzian linebroadening of 1.5 Hz whereas the calculated spectrum is broadened by 5 Hz. Insets show the spinning sidebands and are scaled vertically by a factor of four.

The insets (scaled vertically by a factor of four) show the first-order spinning sidebands which appear with a fairly good S/N ratio and if the centerband were the main interest a faster spin-rate and half the S/N ratio would have been sufficient leading to the possibility of just one phase cycle, i.e., 8 scans (2.7 h). This also makes it relevant to consider adding a suitable amount of paramagnetics into the sample in order to reduce the longitudinal but not the transverse relaxation. For natural samples this may not be necessary as paramagnetics often are present. If the experiments then are performed at high magnetic field strength the width of the central transition is narrowed and it is possible to run the experiments at a lower spin-rate and thereby to use a rotor with a larger volume. The spin-rate just has to be fast enough to separate the centerband from the spinning sidebands of the central transition. Using this approach it is anticipated that ^{17}O NMR in natural abundance would be within reach for a wide range of silicates and oxides.

In the present case the chemical shielding anisotropy (CSA) is going to be determined and therefore the spinning sidebands are of special interest because they are more sensitive to this interaction than the centerband [3]. By iterative fitting employing real-time pulses the quadrupole coupling constant (C_Q), the asymmetry parameter for the quadrupole tensor (η_Q), the isotropic chemical shift (δ_{iso}), the chemical shielding (δ_σ), the asymmetry parameter for the chemical shielding tensor (η_σ) along with the relative orientation of the two tensors given by the Euler angles $\Omega_{\text{PC}}^\sigma (= (\alpha_{\text{PC}}^\sigma, \beta_{\text{PC}}^\sigma, \gamma_{\text{PC}}^\sigma))$ are determined. The calculations in Figs. 1a,c show the effect of the CSA on the intensities of the spinning sidebands. The calculated spectrum in (a) employ the parameters obtained by iterative fitting which are $C_Q = 5.21 \text{ MHz}$, $\eta_Q = 0.19$, $\delta_{\text{iso}} = 43.0 \text{ ppm}$, $\delta_\sigma = 52 \text{ ppm}$, $\eta_\sigma = 0.62$ and $\Omega_{\text{PC}}^{\text{PC}} = (91, 0, 179)^\circ$ whereas no contribution from the CSA is included in (c) and it is evident that the (a) agrees best with the experimental spectrum. As expected the anisotropic parameters are close to the ones determined for the other SiO_2 polymorph, α -cristobalite, obtained by static echo and single-pulse MAS experiments [10] and a recent study that includes molecular

dynamics [11,12]. Taking dynamics into account at room temperature the parameters for α -cristobalite are given by $C_Q = 5.35$ MHz, $\eta_Q = 0.21$, $\delta_{\text{iso}} = 37.5$ ppm, $\delta_\sigma = 50$ ppm, $\eta_\sigma = 0.9$ having a relative orientation of the two tensors defined by the Euler angles $\Omega_\sigma^{\text{PC}} = (270, 7, 90)^\circ$ [12]. The major differences between the interaction parameters for the two polymorphs are observed for the isotropic chemical shift and the relative orientation of the quadrupole- and CSA-tensors which reflects the different oxygen environments due to different crystal structures. In the analysis of α -quartz effects of dynamics are expected to be less important than for α -cristobalite because the experiments are performed at a temperature 548 K below the α - β phase transition temperature (846 K) in α -quartz compared to around 200 K below for α -cristobalite.

Another nucleus that is very important for NMR analysis of minerals and glasses is ^{29}Si . Some very long longitudinal relaxation times have been reported for ^{29}Si [10,13,15] and the CPMG-MAS technique may provide a valuable tool in this context as well because sensitivity enhancement by an order of magnitude may turn into a reduction of experiment time of several days. Previously the QCPMG-MAS approach has been applied to lineshapes being several kHz broad but in case of spin-1/2 nuclei the isotropic line width is in the range of 100's of Hz and therefore the separation of the spin-echo sidebands have to be adjusted such that $1/\tau_a$ is smaller than the linewidth. Fig. 2 shows ^{29}Si α -cristobalite spectra obtained by single-pulse MAS (a), the MAS spectrum reconstructed from the CPMG-MAS spectrum (b), the CPMG-MAS spectrum (c) itself and the difference between the MAS and the reconstructed spectrum (d). The reconstruction is performed by addition of the half-echoes into only one half-echo such as would be acquired by a single-pulse experiment. That is, if npt points are acquired in the first half-echo the reconstructed FID , FID_r , consisting of npt points is obtained by

$$FID_r(i) = FID(i) + \sum_{k=1}^M (FID(i + 2k \cdot npt) + FID^\dagger(2k \cdot npt - i + 2)),$$

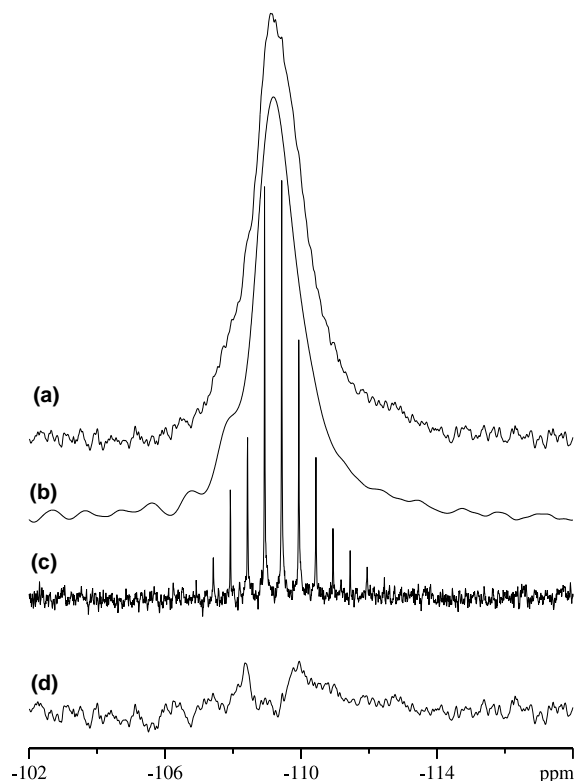


Fig. 2. Experimental ^{29}Si (79.48 MHz) MAS (a) and CPMG-MAS (c) spectra of α -cristobalite. Spectrum (b) is constructed from (c) by co-adding all the half-echoes. The MAS spectrum (a) is acquired using a pulse length of 0.97 μs , a spin-rate of 5.0 kHz, a recycle delay of 10 s and 5400 scans. The CPMG-MAS (c) spectrum is acquired using a recycle delay of 300 s, 8 scans, $(\pi/2)_S = 3.0$ μs , $\tau_1 = \tau_2 = 202.06$ μs , $\tau_3 = \tau_4 = 25.0$ μs , $\tau_a = 25$ ms, $M = 30$, $\tau_d = 20$ ms, using a dwell time of 50.0 μs and a spin-rate of 4949 kHz. Spectrum (d) is the difference between spectrum (a) and (b). The CPMG-MAS spectrum has been apodized by a Lorentzian linebroadening of 1 Hz, whereas 5 Hz have been employed for the MAS and the reconstructed spectrum.

where $i = 1, \dots, npt$ and the \dagger denotes the complex conjugate. The points collected during the τ_d acquisition period is appended to FID_r subsequently to make sure that FID_r is fully decayed such that dc -offset corrections can be made. As can be seen from the difference spectrum (Fig. 2d) the agreement between the MAS spectrum (Fig. 2a) and the reconstructed CPMG-MAS spectrum (Fig. 2b) is good. They both show a single resonance at $-109.1 (\pm 0.1)$ ppm but the linewidth in

the MAS spectrum is 128 Hz compared to 115 Hz for the reconstructed spectrum. Some of this may reflect the effect of different recycle periods in the two experiments. Counting in the experimental time the single-pulse spectrum has been acquired using 15 h whereas the CPMG-MAS used only 40 min. That is, less than a 20th of the MAS spectrum.

Finally a rather challenging sample has been analyzed, a radiation damaged Zircon, Cam26. This sample has been damaged by naturally occurring uranium which substitutes in the Zr site. Along with other radiation damaged Zircons it has been analyzed by X-ray diffraction [14] and single-pulse ^{29}Si MAS NMR [15] with respect to amorphization induced by radiation. Some very long longitudinal relaxation times have been reported for these samples [15] and they therefore serve as excellent test materials for the CPMG-MAS experiment. In Fig. 3 the MAS (a), CPMG-MAS (c) and the reconstructed MAS (b) spectra are displayed. A narrow resonance at -83.3 ppm corresponding to the single Si site in crystalline Zircon and a broad resonance centered around -93 ppm originating from the amorphous part of the sample due to radiation damage are observed in all spectra. Whilst spin-echo sideband spectra are reasonably easy to interpret when they are of crystalline materials, the reconstruction of the single-pulse lineshape for amorphous samples is important because there is no a priori information as to the form of the line in amorphous materials. Also, not to be overlooked, is the familiarity of the spectroscopist with the line shape instead of the spin-echo sideband manifold. Looking at the experiment time and processing the MAS spectrum (Fig. 3a) has been acquired in 45 h and apodized by a Lorentzian linebroadening of 50 Hz whereas the CPMG-MAS and the reconstructed spectrum (Figs. 3c,b) have been apodized by Lorentzian linebroadenings of 1 and 50 Hz, respectively, using only 8 h of acquisition time. The two latter spectra display a similar S/N-ratio as the MAS spectrum even though the CPMG-MAS spectrum required less than a fifth of spectrometer time. This reduction by a factor of five in spectrometer time may be used for faster experiments such as for kinetic work, smaller sample volumes or less concentrated

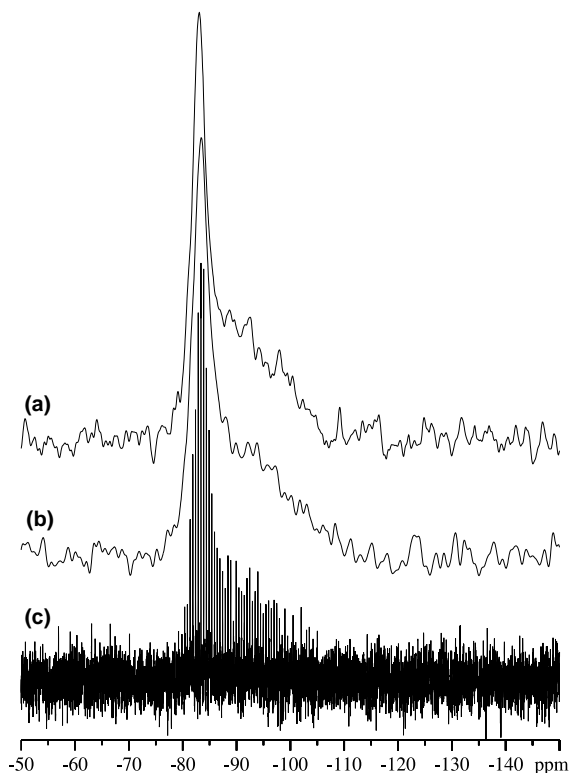


Fig. 3. Experimental ^{29}Si (79.48 MHz) MAS (a) and CPMG-MAS spectra (c) and the reconstructed spectrum (b) of Zircon (Cam26). The MAS spectrum (a) is acquired using a pulse length of $1.0 \mu\text{s}$, a spin-rate of 5.0 kHz, a recycle delay of 270 s and 600 scans. The CPMG-MAS (c) spectrum is acquired using a recycle delay of 3600 s, 8 scans, $(\pi/2)_S = 5.0 \mu\text{s}$, $\tau_1 = \tau_2 = 192.77 \mu\text{s}$, $\tau_3 = \tau_4 = 25.0 \mu\text{s}$, $\tau_a = 25$ ms, $M = 30$, $\tau_d = 10$ ms, using a dwell time of $50.0 \mu\text{s}$ and a spin-rate of 5188 kHz. Lorentzian linebroadening of 1 Hz have been applied to the CPMG-MAS spectrum, whereas 50 Hz have been employed for the reconstructed MAS and the MAS spectrum.

samples which extends the applicability of ^{29}Si NMR as a strong analytical tool.

4. Conclusions

In conclusion it has been demonstrated that sensitivity gains by at least an order of magnitude obtained using a rotor synchronized train of refocusing π -pulses during acquisition makes it feasible to acquire spectra of nuclei with long longitudinal relaxation times. For ^{17}O this ap-

proach points toward a general method for observation of ^{17}O and other quadrupolar nuclei with moderate nuclear quadrupole moment such as ^{43}Ca in natural abundance. The increased sensitivity in the ^{29}Si NMR spectra broadens the range of Si and other spin-1/2-containing compounds to be studied despite their long longitudinal relaxation times. The reduction of experiment time for the ^{29}Si experiments points at the (Q)CPMG-MAS experiment as a general acquisition approach not only to broader lineshapes obtained for half-integer quadrupolar nuclei but also to narrower resonances for any NMR active nucleus.

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