Communication

Site-selective QPASS for the isolation of large quadrupolar coupling environments

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Abstract

Spectral editing of high spinning rate quadrupolar powder patterns observed using the QPASS experiment was achieved through the coupling of QPASS with the selective $\pi/2$-RAPT enhancement sequence. The resulting $\pi/2$-RAPT-QPASS sequence yields spectra that are dominated by the powder patterns form sites with large quadrupolar couplings thus reducing the overlap of patterns from multiple sites of different symmetry in a material. The ^{93}Nb isotropic chemical shifts and quadrupolar coupling parameters were determined for the two niobium crystallographic sites in the layered $KCa_2Nb_3O_{10}$. The asymmetric surface site in the structure was selectively enhanced and easily fit to second-order quadrupolar powder pattern with this method.
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1. Introduction

The use of solid-state NMR to study inorganic materials increasingly depends on the capability to observe and quantify the environments associated with quadrupolar nuclei in these materials. As quadrupolar nuclei make up about 75% of the observable NMR isotopes and consist of many of the elements found in inorganic materials, the need for the characterization of these materials from a quadrupolar perspective becomes obvious. Over the past decade or so, numerous techniques, such as MQMAS [1], DAS [2], DOR [3], and STMAS [4], have been developed to produce higher resolution spectra that permit the determination of important NMR parameters related to half-integer quadrupolar nuclei. These pulse sequences are generally successful with quadrupolar interactions that are of moderate size, but the efficiency of multiple-quantum excitation and the effective averaging by mechanical spinning diminish as the quadrupolar interaction grows larger.

The limitation to moderate quadrupolar interactions means that only nuclei with small quadrupolar moments, in small to moderate electric field gradients, or with low nuclear spin numbers can be studied effectively. In addition to limiting the possible quadrupolar nuclei that can be studied, the types of environments encountered in materials that can be studied are limited as well. Nuclei situated at surface sites in a material can experience extremely large electric field gradients due to the asymmetry of the surface environment. Under these conditions, even isotopes with low nuclear spins and moderate nuclear quadrupole moments will still have large quadrupolar couplings. As many materials today capitalize on the high surface area and high surface to volume ratios found in nanomaterials, NMR approaches that can characterize these important surface sites become crucial.

One solution to the difficulties of large quadrupolar couplings is to use a larger static magnetic field, as the magnitude of the second-order quadrupolar coupling is inversely proportional to the magnetic field. However, to get a significant reduction in the interaction, in many cases a doubling of the field is necessary. With current solid-state NMR systems already operating at 400 and 500 MHz, a significant

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increase in field would be possible only with specialized systems such as those available at national laboratories. In this situation, routine or systematic studies become limited due to access. Larger magnetic fields also would increase any chemical shift anisotropy present of the nuclei, as the interaction is proportional with the field. Increases in chemical shift anisotropy would require higher spinning rates to gain high resolution and to minimize overlap between isotropic peaks and sidebands.

Another approach to obtain higher resolution NMR data for quadrupolar nuclei is through the QPASS pulse sequence [5]. QPASS permits the observation of second-order quadrupolar powder patterns under reconstructed infinite magic angle spinning rates. The two-dimensional sequence permits the observation of these nuclei using moderate magnetic field strengths and moderate spinning rates. Since the final spectrum, produced through the summation of the sheared two-dimensional QPASS spectrum, is the equivalent of an infinite spinning rate spectrum, the observed powder pattern is free of influences from chemical shift anisotropy. The resulting one-dimensional spectrum can be fit by only considering the isotropic chemical shift and second-order quadrupolar interaction.

While QPASS creates higher resolution spectra of quadrupolar nuclei, the method does suffer from low signal intensity and the potential of overlap of signals from multiple sites. Since the isotropic chemical shift difference between different sites in a material can be less than the size of the second-order quadrupolar powder pattern, overlap of the multiple patterns becomes inevitable. The lack of a second dimension by which to separate the signals from different sites limits the utility of the QPASS technique for complex materials. Selective suppression or excitation of the signal from specific sites could simplify the complicated QPASS spectrum of a material. Double resonance methods such as cross-polarization could possibly achieve selective excitation of nuclei in the QPASS experiment. However, the use of double resonance requires the presence of a second abundant hetero-nucleus that is in close enough proximity to create the dipolar interaction necessary for polarization transfer. These necessary hetero-nuclei may not always be present in many inorganic materials.

A preferable approach would be to suppress or enhance signals based on the environment of the nuclei. This approach can be achieved through population transfer from satellite transitions to the central transition of the quadrupolar nucleus. This kind of signal enhancement is possible with rotor-assisted population transfer, RAPT [6,7], which utilizes off-resonance excitation coupled with sample rotation to increase the central transition signal. Recently, modified versions of the RAPT sequence have been created to selectively suppress the signal from nuclei based on the magnitude of the quadrupolar coupling [8]. While increases in signal intensity are not observed with these modified sequences, the reduction or elimination of certain quadrupolar powder patterns is observed.

In this communication, we demonstrate the utility of coupling selective RAPT pulse sequences with the QPASS sequence to clarify spectra that result from the overlap of quadrupolar powder patterns. In particular, we use the $\pi/2$-RAPT sequence with a multiple-rotor cycle version of QPASS [9] to elucidate the quadrupolar information for the ^{93}Nb site in a layered niobium oxide material, $KCa_2Nb_3O_{10}$. The $\pi/2$-RAPT pulse sequence selectively removes the signal from small quadrupolar coupling sites, leaving behind only the large quadrupolar coupling environments with which the QPASS sequence can create high spinning rate central transition powder patterns. This combination effectively separates the signals from the two crystallographically different environments in the layered niobate, which are expected to have different couplings as the two sites have different local symmetries.

2. Results

The enhancement of the ^{93}Nb Hahn echo signal using the standard RAPT enhancement sequence in place of the $\pi/2$ pulse was measured as a function of the frequency offset of the RAPT saturation pulse train. The maximum in the enhancement is related to the magnitude of the quadrupolar coupling constant (C_Q) of the site, as $v_{max} \approx 3 C_Q/(4I(2I-1))$ [7] where I is the spin of the nucleus. For $KCa_2Nb_3O_{10}$ the observed maximum was found to be approximately 800 kHz (Fig. 1). In order to suppress the signal from the smaller quadrupolar coupling site, the offset for the $\pi/2$-RAPT sequence must be set to a value above $2 * v_{max}$ of the smaller coupling site [8]. Based on the observed maximum, an offset value of 1.6 MHz was used. A spectrum from the $\pi/2$-RAPT-QPASS experiment was collected at an effective spinning rate of infinity and is shown in Fig. 2A. Using the DMFIT2005 software package [10], the resulting central transition powder pattern from the selective experiment could be fit with a powder pattern with a quadrupolar coupling constant value of 30.6 ± 0.8 MHz and an asymmetry parameter of 0.3; the fit is shown in Fig. 2B. The isotropic chemical shift derived from the fit was -976 ± 2 ppm. The chemical shift values were reference to $NbCl_5$ in wet acetonitrile (0 ppm). A single set of parameters was sufficient to fit the observed data.
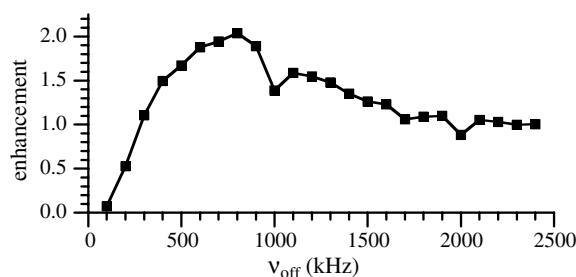

Fig. 1. Signal enhancement of the ^{93}Nb signal versus frequency offset of the Gaussian pulse train in the RAPT experiment on $KCa_2Nb_3O_{10}$.
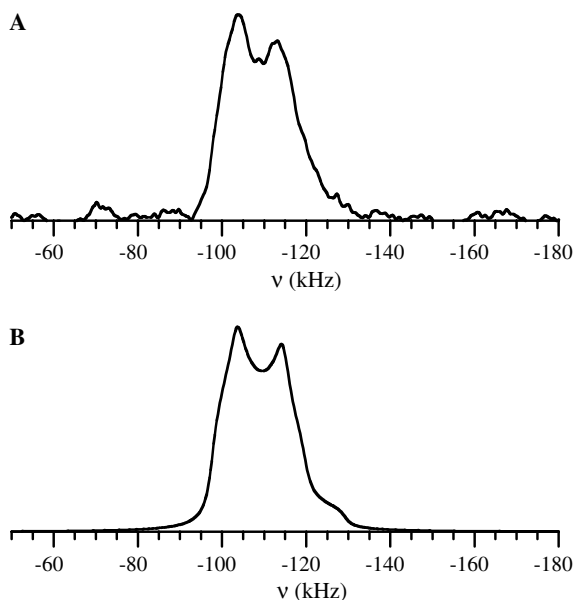
Fig. 2. (A) Final spectrum from $\pi/2$-RAPT-QPASS experiment on the ^{93}Nb nuclei in $KCa_2Nb_3O_{10}$ and (B) simulated quadrupolar powder pattern fit of the experimental data.

A non-selective RAPT-enhanced QPASS data set was collected for the $KCa_2Nb_3O_{10}$ sample using an offset of 700 kHz. The resulting one-dimensional spectrum had an effective spinning rate of infinity and is shown in Fig. 3A. Using the chemical shift and quadrupolar parameters from the selective experiment, the remaining signal in the QPASS spectrum was fit with a quadrupolar coupling constant of 20.7 ± 0.3 MHz, a quadrupolar asymmetry parameter of 0.6, and an isotropic chemical shift of -998 ± 2 ppm. The total simulated central transition pow-
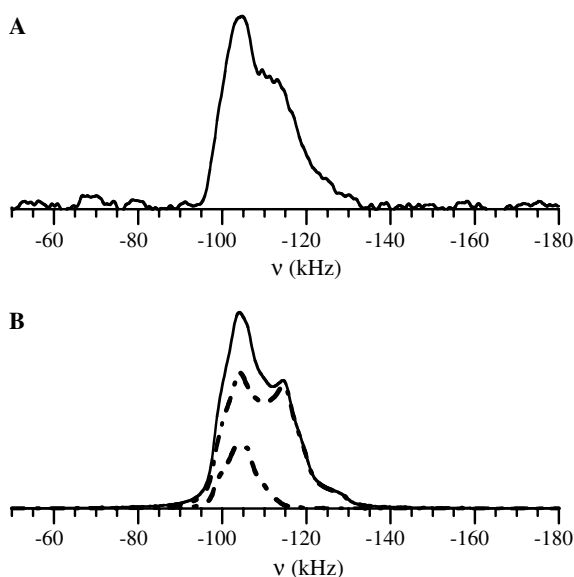

Fig. 3. (A) Final spectrum from RAPT-QPASS experiment on the ^{93}Nb nuclei in $KCa_2Nb_3O_{10}$ and (B) simulated quadrupolar powder pattern fit of the experimental data, total fit (solid line) fits for individual sites (dashed lines).

der pattern and the two individual fits are shown in Fig. 3B. Based on the intensities of the two powder patterns in the fit, the population ratio of the large coupling site to the small coupling site is 80:20.

3. Discussion

$KCa_2Nb_3O_{10}$ is a member of the Dion–Jacobson family of layered perovskites. The structure consists of triple perovskite layers separated by a single layer of potassium cations [11]. The perovskite layer consists of niobia octahedra that share vertices and calcium cations nested between the connected polyhedra in 12-coordinate sites. In this structure, there are two distinct octahedral sites for the niobium cations, one site at the interface of the layers and one in the center of the layers. A 2:1 ratio exists between the population of sites at the interface and sites in the center of the layers. The niobium cations in the interface site sit in distorted environments with axial Nb–O bonds that have a length of 1.75 Å for the bonds that point away from the layer and 2.39 Å for the bonds that point toward the layer. The remaining four bonds have lengths in the range of 1.97–2.02 Å. As a result, the niobium site at the interface could almost be considered five-coordinate if the long Nb–O bond is ignored. The site in the center of the layer is more isotropic than the interface site. Six Nb–O bonds that range in length from 1.91 to 2.02 Å surround the niobium cation at this site. While the site is more isotopic, X-ray diffraction has observed some disorder among the NbO_6 octahedra in the center of the layers.

The layered niobate is an interesting test material for the selective QPASS technique. The distortion in the niobium site at the interface of the layers is commonly observed in other layered compounds [12]. The shortened Nb–O bond is considered to be highly acidic and partially responsible for the acid catalytic capabilities of these layered compounds. The niobium site in the center is only a few bond lengths removed from the surface and yet it has an entirely different local structure. Differentiating between the signals from these two sites becomes crucial if studies of properties derived from the structure of the surface are to be made.

The selective $\pi/2$-RAPT-QPASS experiment produced a central transition powder pattern (Fig. 2A) that was substantially different from the pattern observed for the non-selective QPASS experiment (Fig. 3A). The lineshape that resulted from the final spectrum was easily fit and yielded parameters that are indicative of a highly distorted quadrupolar site ($C_Q = 30.5$ MHz) compared to couplings typically observed for bulk niobates such as $LiNbO_3$ and $NaNbO_3$ which have values around 22 MHz [13]. In the fitting of the quadrupolar lineshape, chemical shift anisotropy was not needed to fully describe the observed powder pattern. It should be noted that a quadrupolar coupling of $\sim$31 MHz has a static linewidth of $\sim$90 kHz; however, the MAS echo spectrum of the sample spinning at 20 kHz does not show well-resolved central transition powder patterns (Fig. 4). The large powder pattern observed
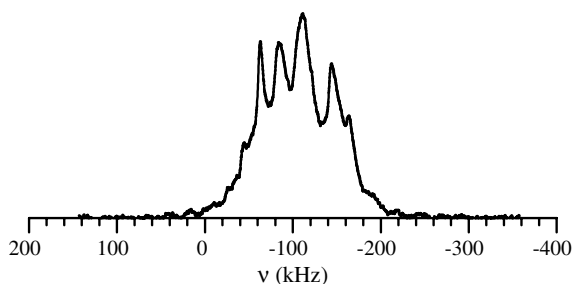
Fig. 4. ^{93}Nb Hahn echo spectrum of KCa$_2$Nb$_3$O$_{10}$ spinning at 20 kHz.

probably does have some influence from chemical shift anisotropy, which contributes to an increase beyond a 90 kHz linewidth.

Using the information from the selective experiment, a fit of the non-selective QPASS spectrum was feasible. The fit yielded parameters that described a more isotropic site ($C_Q = 20.7$ MHz) as expected based on the known crystal structure for KCa$_2$Nb$_3$O$_{10}$. Again chemical shift anisotropy parameters were not needed to describe the second site. The population ratios of the two signals followed the trend that is observed in the crystal structure with the ratio between the large and small coupling site at 4:1. The non-selective experiment did overestimate the population of the large coupling site but the intensity information must be used with some caution as the non-selective RAPT sequence will increase the signal intensity from the two sites differently. Depending on the offset value, it is expected that the signal intensities will be modified slightly as one site will be closer to its individual enhancement maximum compared to the other. The only effective way to avoid the population discrepancies is by using the QPASS sequence without any enhancement methods. However, this would substantially increase the data collection time needed to achieve signal to noise ratios similar to what are observed with the enhanced sequences. Nevertheless, the RAPT-QPASS method did give a good sense of which niobium environment is in the majority. Additional experiments with different offset values could be performed to look at trends in the population ratios to better determine the actual ratio.

Both the RAPT and π/2-RAPT sequences could be coupled easily with the QPASS technique through the replacement of the initial π/2 pulse with these sequences. Due to the high spinning rates used in the experiment, the standard QPASS sequence in which the nine π pulses occur over the period of one rotor cycle could not be used. The pulse lengths would be too long for any significant delay between pulses to be present. A multiple-rotor cycle version of the QPASS sequence was used in which the pulses are distributed over three rotor cycles [9]. Higher power, shorter pulses could not be used since all the pulses in the QPASS sequence needed to be selective for the central transition only, and thus of low power. The original multiple-rotor cycle QPASS sequence utilized 16 sets of timings for the delays between the π pulses. The data set collected using

the non-selective RAPT-QPASS experiment utilized this set of timings due to the good signal intensity gained through the RAPT enhancement. The selective π/2-RAPT-QPASS experiment did not have the same gain in intensity, which was sacrificed for selectivity, and a shorter sequence of 8 sets of timings was used. Use of a reduced number of sets has been demonstrated as a means to improve signal in the QPASS experiment without lengthening the data collection times [14]. In the case of the KCa$_2$Nb$_3$O$_{10}$, no significant residual sidebands were observed with the smaller set of timings.

4. Conclusions

Spectral editing of multiple quadrupolar sites to yield selective information is possible through the coupling of selective RAPT enhancements with the QPASS experiment. For the ^{93}Nb nuclei in KCa$_2$Nb$_3$O$_{10}$, it was possible to separate the quadrupolar powder patterns for the two metal sites in the material based on the magnitude of the quadrupolar coupling. The use of QPASS with selective RAPT produced powder patterns that are dependent on quadrupolar coupling alone, thus simplifying the analysis of the final patterns. This approach is not limited to ^{93}Nb nuclei but is potentially useful for any half-integer nuclei with large quadrupolar couplings particularly in cases where numerous quadrupolar environments exist.

5. Experimental

The layered niobate was prepared via microwave synthesis. A mixture of K$_2$SO$_4$, CaSO$_4$, and Nb$_2$O$_5$ was pressed into a pellet with a mole ratio of 10:2:3 for K:Ca:Nb. The pellet was heated in a bed of activated charcoal (Darco G-60) in a porcelain crucible, which in turn was placed in a sand bed to absorb the emitted heat from the crucible. The materials were irradiated in a 1200 W domestic microwave oven for 5–10 min at 70% power to produce the desired phase. The phase was recovered from the potassium sulfate flux through washing with distilled water. The sample was allowed to dry at room temperature. The sample identity was determined using X-ray powder diffraction on a Bruker AXS D8 Focus diffractometer and the diffraction pattern was compared to literature values [11].

All data were collected using a 400 MHz Unity Inova spectrometer with a ^{93}Nb resonance frequency of 97.74 MHz. For both the MAS and RAPT-QPASS experiments, the samples were spun at 20 kHz using a Chemagnetics 2.5 mm, double resonance MAS probe. Selective pulses used in RAPT and QPASS pulse sequences both had radiofrequency field strengths of 20 kHz yielding selective π/2 and π pulse lengths of 2.5 and 5.0 μs. The pulse train in the non-selective RAPT-QPASS sequence had a radiofrequency strength of ∼83 kHz and a pulse length of 12 μs with a σ of 1.2 μs for the Gaussian pulses. The pulse

train in the selective π/2-RAPT-QPASS sequence had a radiofrequency strength of ∼83 kHz and a pulse length of 14 μs with a σ of 2.975 μs for the Gaussian pulses. Frequency offsets of 700 kHz were used for the non-selective experiment and 1.6 MHz for the selective experiment. An additional rotor period was added to the last delay to allow for whole echo acquisition. A phase cycle based on cogwheel principles [15,16] was used to reduce the minimum number of scans to 40. A recycle delay of 0.6 s was used for the experiments. 6400 transients per step were collected in the RAPT-QPASS experiment and 16,000 transients per step were collected in the π/2-RAPT-QPASS experiment. The chemical shift values were reference to $NbCl_5$ in wet acetonitrile (0 ppm). All data were processed using the RMN processing program for the Macintosh [17]. Fitting of the final QPASS spectra was conducted using DMFIT2005 [10].

Acknowledgments

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